## Experimental Section

The C-carbethoxyformazans were obtained by standard procedures.[10]

N,N′-Bis(4-methoxyphenyl)-C-carbethoxyformazan had mp 131–132°. *Anal.* Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.44; H, 5.59; N, 15.91.

N,N′-Bis(4-nitrophenyl)-C-carbethoxyformazan had mp 208–210°. *Anal.* Calcd for $C_{18}H_{20}N_6O_6$: C, 49.74; H, 3.65; N, 21.75. Found: C, 49.68; H, 3.53; N, 22.45.

The ¹⁵N-labeled N,N′-diphenyl-C-carbethoxyformazan and N,N′-bis(3,5-dichlorophenyl)-C-carbethoxyformazan were prepared by the same procedure using $Na^{15}NO_2$ for the diazotization of aniline or 3,5-dichloroaniline.

The ¹⁵N-labeled N,N′,C-triphenylformazan was prepared by

(10) H. von Pechmann, *Chem. Ber.*, **25**, 3175 (1892); F. A. Neugebauer, *Monatsh. Chem.*, **98**, 241 (1967).

the reaction of labeled benzene diazonium chloride (aniline and $Na^{15}NO_2$) with malonic acid.[11]

The tetrazolinyl radicals were generated by reaction of 0.2 ml of the formazan (0.001 $M$) in benzene with 0.2 ml of a 0.005 $M$ solution of tetra-*p*-tolylhydrazine in benzene. The mixture was deoxygenated in a fused silica esr cell by a stream of prepurified nitrogen for 10 min. After closing the cell the mixture was heated to 60° for 10 sec (or the mixture was allowed to stand for 30 min at room temperature). The red-brown color of the solution changed into greenish brown after completion of the reaction.

**Registry No.**—N,N′-Bis(4-methoxyphenyl)-C-carbethoxyformazan, 16626-70-3; N,N′-bis(4-nitrophenyl)-C-carbethoxyformazan, 16626-71-4.

(11) F. A. Neugebauer and B. Küchler, *Ann. Chem.*, **706**, 104 (1967).

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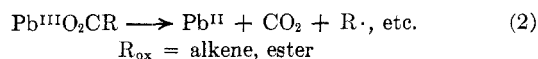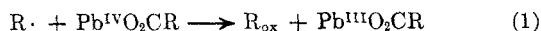# Solvent Effects on the Oxidation of Alkyl Radicals by Lead(IV) and Copper(II) Complexes

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Oxidative decarboxylation of acids by lead(IV) acetate has been used to study solvent effects on the oxidation alkyl radicals by $Pb^{IV}$ species. In the presence of copper catalyst, the rapid oxidation of alkyl radicals by $Cu^{II}$ overwhelms the oxidation by $Pb^{IV}$. In both cases, alkenes (elimination) and alkyl esters (substitution) are products of electron-transfer oxidation of alkyl radicals by either $Pb^{IV}$ or $Cu^{II}$ oxidants. Homoallylic $C_4H_7$ radicals were chosen for study, since they represent optimum examples in which to observe these competing oxidative processes. Oxidative elimination of cyclobutyl radicals affords cyclobutene, whereas oxidative substitution produces a mixture of cyclobutyl, cyclopropylmethyl, and allylcarbinyl esters. Solvent effects on oxidative elimination and substitution of cyclobutyl radicals by $Pb^{IV}$ as well as $Cu^{II}$ have been scrutinized in order to differentiate these oxidants. $Pb^{IV}$ is rather insensitive to solvent changes, and oxidative substitution is the preferred course of oxidation. The oxidation of cyclobutyl radicals by $Cu^{II}$ species is highly dependent on solvent. In ethyl acetate or benzene, oxidative elimination to cyclobutene persists, whereas in acetonitrile oxidative substitution results. The dichotomy between oxidative elimination and substitution is resolved by a general mechanism which generally pertains to the oxidation of alkyl radicals by $Pb^{IV}$ and $Cu^{II}$.
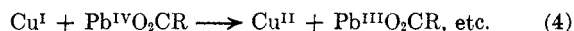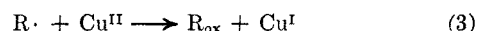
The decarboxylation of various acids by lead(IV) tetraacetate in benzene solutions has been induced thermally and photochemically.[1] A free-radical chain process prevails under these conditions, and the relevant propagation sequence has been postulated[1-3] as shown in eq 1 and 2. The kinetic chain length of the

$$R\cdot + Pb^{IV}O_2CR \longrightarrow R_{ox} + Pb^{III}O_2CR \qquad (1)$$

$$Pb^{III}O_2CR \longrightarrow Pb^{II} + CO_2 + R\cdot, \text{ etc.} \qquad (2)$$
$$R_{ox} = \text{alkene, ester}$$

decarboxylation is principally related to the facility of the oxidation step (eq 1). Decarboxylation of primary and secondary acids are relatively slow and exhibit short chain lengths. In contrast, tertiary and those acids which yield radicals such as benzyl and allyl, decarboxylate readily and have long chain lengths.[1,4] Generally speaking, primary and secondary alkyl radicals are not readily oxidized by $Pb^{IV}$, and alkanes (RH) usually result during decarboxylation of such acids by $Pb^{IV}$. Long chain lengths in decarboxylation are primarily correlated with high yields of oxidation products ($R_{ox}$).

By the same token, the decarboxylation of primary and secondary acids is markedly catalyzed by copper

salts,[2,5] whereas the decarboxylation of tertiary and related acids is little affected under the same conditions.[4] Copper catalysis has been attributed to the efficient interception of alkyl radicals by $Cu^{II}$ (eq 3) and subsequent reduction of $Pb^{IV}$ (eq 4). In this manner,

$$R\cdot + Cu^{II} \longrightarrow R_{ox} + Cu^{I} \qquad (3)$$

$$Cu^{I} + Pb^{IV}O_2CR \longrightarrow Cu^{II} + Pb^{III}O_2CR, \text{ etc.} \qquad (4)$$

the comparatively slow oxidation of primary and secondary alkyl radicals by $Pb^{IV}$ (eq 1) can be circumvented, and long kinetic chain lengths for decarboxylation and high yields of oxidation products ensue. From these and other observations, it has been concluded that the rates of oxidation of alkyl radicals by $Pb^{IV}$ are roughly in the following order: $Ph_3C\cdot >$ allyl $> t$-alkyl $\gg sec$-alkyl $>$ primary alkyl.[1,3,4]

The kinetics and products of oxidation of alkyl radicals by $Cu^{II}$ can also be studied by an independent method using diacyl peroxides as the source of radicals.[6] Such measurements have shown that the rates of oxidation of alkyl radicals by $Cu^{II}$ are very fast ($k_2 > 10^8$ l. $m^{-1}$ sec$^{-1}$) and are generally not highly dependent on structure.[7]

Studies of the oxidation of alkyl radicals by both $Pb^{IV}$ and $Cu^{II}$ using these methods indicate that two princi-

(1) J. Kochi, J. Bacha, and T. Bethea, *J. Amer. Chem. Soc.*, **89**, 6538 (1967).
(2) J. Kochi, *ibid.*, **87**, 3609 (1965).
(3) In the following presentation, coordination around Pb and Cu will not be given explicitly, except where pertinent to the discussion.
(4) J. Bacha and J. Kochi, *J. Org. Chem.*, **33**, 83 (1968).

(5) J. Bacha and J. Kochi, *Tetrahedron*, **24**, 2215 (1968).
(6) J. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963); J. Kochi and A. Bemis, *Tetrahedron*, in press.
(7) J. Kochi and R. Subramanian, *J. Amer. Chem. Soc.*, **87**, 4855 (1965).

TABLE I
THERMAL AND PHOTOCHEMICAL DECARBOXYLATION OF CYCLOBUTANECARBOXYLIC ACID[a]

| Initiation | Solvent PhH/HOAc (v/v) | $Cu^{II}$, M | Py, M | □ | □ | Total acetate | □–OAc (6) | □–OAc | ▽–OAc | □–Ph | Sum of $C_4H_7$[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Thermal | 95/0 | 0.0051 | 0 | 67 | 0.5[d] | 4 | (6) | (43) | (51) | N.D. | 72 |
| Photochem | 95/0 | 0.0051 | 0 | 75 | 0.5 | 3 | (6) | (42) | (52) | N.D. | 79 |
| Thermal | 75/20 | 0.0051 | 0 | 38 | 0.4[d] | 15 | (6) | (41) | (53) | N.D. | 53 |
| Photochem | 75/20 | 0.0051 | 0 | 58 | 0.4 | 17 | (5) | (41) | (54) | N.D. | 75 |
| Thermal | 95/0 | 0 | 0.10 | 1 | 4 | 37[e] | (5) | (46) | (49) | 31 | 73 |
| Photochem | 95/0 | 0 | 0.10 | 4 | 8 | 44[f] | (5) | (44) | (51) | 19 | 75 |
| Thermal | 15/20[g] | 0.0051 | 0.066 | 13 | 2 | 36 | (6) | (42) | (52) | N.D. | 51 |
| Photochem | 15/20[g] | 0.0051 | 0 | 2 | 8 | 64 | (3) | (47) | (50) | N.D. | 74 |

[a] In solutions containing 0.10 M $Pb^{IV}$ and 0.52 M cyclobutanecarboxylic acid (5% by vol.). Thermal at 80°, photochemical at 30°, and 3500 Å. [b] Based on moles/mole of $Pb^{IV}$ irrespective of oxidation state. Values in parentheses represent relative yields. N. D. = not determined. [c] Sum of all $C_4H_7$ fragments does not represent optimum when all products not analyzed. [d] Ca. 0.5% 1,3-butadiene. [e] Includes 15% acetates and 22% cyclobutanecarboxylates (cyclobutyl, 42%, cyclopropylmethyl, 54%, and allylcarbinyl, 4%). [f] Includes 17% acetates and 27% cyclobutanecarboxylates (cyclobutyl, 41%, cyclopropylmethyl, 55%, and allylcarbinyl, 4%). [g] Acetonitrile, 60%.

pal types of products are formed: alkenes and alkyl esters. These products are *formally* derived by 1-equiv oxidation of alkyl radicals according to the standard (half-cell) reactions given by eq 5 and 6, respectively.

I. Oxidative elimination
$$R\cdot \longrightarrow R(-H) + H^+ + \epsilon \qquad (5)$$
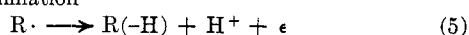
II. Oxidative substitution
$$R\cdot + HO_2CR \longrightarrow RO_2CR + H^+ + \epsilon \qquad (6)$$
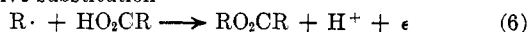
Oxidation of most primary and secondary alkyl radicals by $Cu^{II}$ usually affords alkene (eq 5).[8] Allylic radicals on oxidation produce only esters (eq 6),[9] but benzylic,[10] homoallylic,[11] and *t*-alkyl radicals usually form a mixture of elimination and substitution products. Furthermore, alkenes generated in the former cases are generally free from rearranged isomers, but esters from oxidative substitution in the second category are often extensively rearranged. The oxidations (I and II) have been classified as *electron-transfer* processes,[12] and two parallel routes have been postulated.[11]

Some preliminary studies (*vide infra*) showed that the copper-catalyzed oxidative decarboxylation of cyclobutanecarboxylic acid by $Pb^{IV}$ was highly dependent on solvent. Thus, in acetonitrile a mixture of homoallylic esters was generated in excellent yields (>70%), but in benzene solutions under similar conditions, cyclobutene was formed in 75% yield. In this paper, we wish to scrutinize the effect of solvents generally on both oxidative decarboxylation of acids by $Pb^{IV}$ and the decarboxylation catalyzed by $Cu^{II}$ salts. Solvent effects are operative in the former through oxidation of alkyl radicals by $Pb^{IV}$ species (eq 1), and in the latter through oxidation by $Cu^{II}$ species (eq 3). The homoallylic carboxylic acids, particularly cyclobutanecarboxylic acid,[13] were especially selected for detailed study because they presented optimum opportunities to examine the effects of solvent on a

(8) H. DeLaMare, F. Rust, and J. Kochi, *J. Amer. Chem. Soc.*, **85**, 1437 (1963).
(9) J. Kochi, *ibid.*, **84**, 774 (1962); **84**, 3271 (1962).
(10) J. Kochi and R. Gilliom, *ibid.*, **86**, 5251 (1964).
(11) J. Kochi and A. Bemis, *ibid.*, in press.
(12) J. Kochi, *Rec. Chem. Progr.*, **27**, 209 (1966).
(13) (a) Oxidative decarboxylation of cyclobutanecarboxylic acid by $Pb^{IV}$ was reported to give a mixture of cyclobutyl, allylcarbinyl, and cyclopropylmethyl acetates. G. Büchi and J. Marvel [quoted in ref 13 of a paper by E. Corey and J. Casanova, *J. Amer. Chem. Soc.*, **85**, 167 (1963)]. (b) For convenience, we describe cyclobutyl, cyclopropylmethyl, and allylcarbinyl as *homoallylic derivatives*.

number of reactions, which often occur concurrently during oxidation of radicals, *viz.*, oxidative elimination I, oxidative substitution II, rearrangement, hydrogen transfer (reduction to alkanes), and aromatic substitution. In addition, various solvents facilitate decarboxylation of acids by $Pb^{IV}$ even at room temperatures (*vide infra*). It is hoped that these studies will shed light on the general mechanism of the oxidation of alkyl radicals by $Pb^{IV}$ as well as $Cu^{II}$ complexes.

## Results

A standard procedure was adopted for the study of solvent variation on oxidative decarboxylation. A stock solution of 0.1 M lead(IV) tetraacetate and 0.4 M carboxylic acid ($RCO_2H$) was made up with acetic acid and the appropriate solvent. In most cases, acetic acid and the other component constituted 10 and 86% by volume, respectively, of the reaction mixture. Small variations in acetic acid concentration had only minor effects on the reaction. Acetic acid served the very useful purpose of diverting the alkyl radical on oxidative substitution to alkyl acetates, which were stable and could be readily analyzed. In general, the ratio of the yields of alkyl acetates and alkyl esters (derived from the parent acid, $RCO_2H$) were obtained predictably, simply on the basis of the mole fraction of acetic acid and $RCO_2H$. Competition between acetic acid

$$RCO_2H + Pb^{IV} + HOAc \longrightarrow$$
$$[ROAc + RO_2CR] + CO_2 + Pb^{II} + 2H^+ \qquad (7)$$
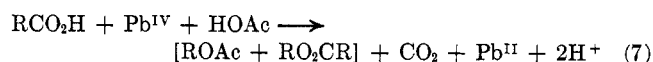
and cyclobutanecarboxylic acid in the decarboxylation step (eq 2) was not serious in 10% (by volume) acetic acid solutions. However, it may have contributed to the low yield of products obtained by the decarboxylation of allylacetic and cyclopropylacetic acids, which as primary acids suffer from this competition.[2,4,5]

**Photochemical and Thermal Decarboxylation of Cyclobutanecarboxylic Acid by $Pb^{IV}$.**—Decarboxylation of cyclobutanecarboxylic acid by $Pb^{IV}$ was carried out thermally at 80°[2] in a thermostated bath or photochemically at 30° with irradiation at 3500 Å.[1] These reactions were studied in the presence and absence of $Cu^{II}$ complexes and pyridine after thorough purging with argon. The principal products obtained under these conditions (Table I) were cyclobutane, cyclobutene, and a mixture of homoallylic acetates and cyclo-
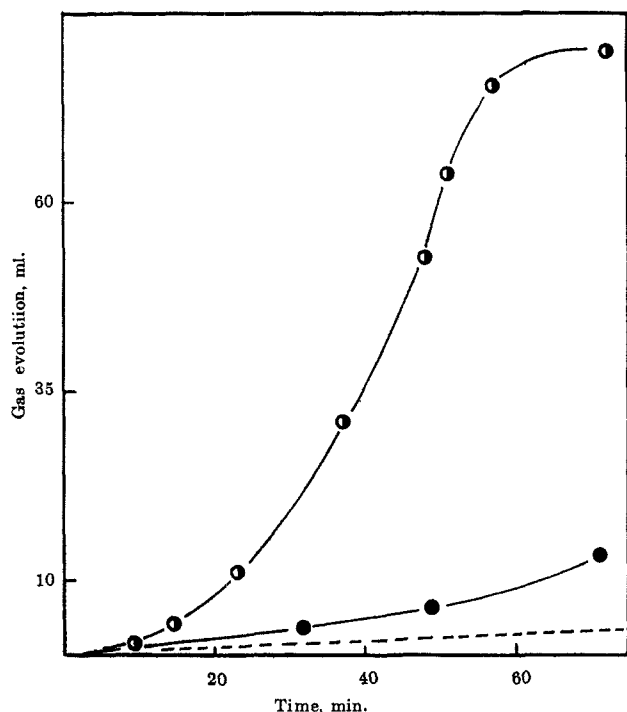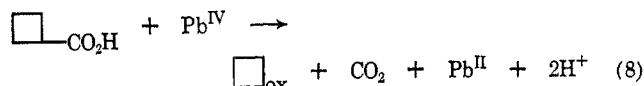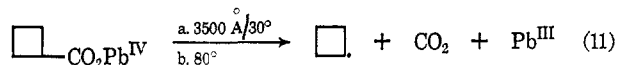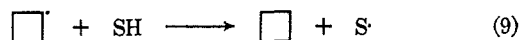
Figure 1.—Thermal decarboxylation of 0.46 $M$ cyclobutanecarboxylic acid with 0.10 $M$ lead(IV) acetate in benzene at 80°: $\mathrm{o}$, 0.0051 $M$ copper(II) acetate; $\bullet$, 0.10 $M$ pyridine; dotted line, no additive.

butanecarboxylates. In most cases, the material balance of the cyclobutyl moiety was greater than 70% based on the stoichiometry given in eq 8. All of these

$$\square\!\!-\!CO_2H + Pb^{IV} \longrightarrow$$
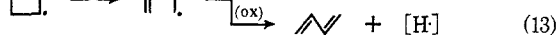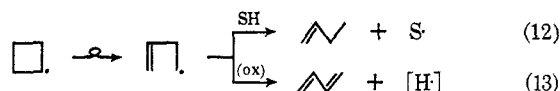$$\square_{ox} + CO_2 + Pb^{II} + 2H^+ \quad (8)$$

products, with the exception of cyclobutane and cyclobutylbenzene (obtained only in benzene), resulted from oxidation of cyclobutyl radicals. The latter two were formed by attack on solvent by hydrogen abstraction (eq 9)[14] or substitution (eq 10),[2] and were especially

$$\square\cdot + SH \longrightarrow \square + S\cdot \quad (9)$$

$$\square\cdot + \bigcirc \xrightarrow{(ox)} \square\!\!-\!\!\bigcirc + [H\cdot] \quad (10)$$

$$\square\!\!-\!CO_2Pb^{IV} \xrightarrow[b.\,80°]{a.\,3500\,\overset{o}{A}/30°} \square\cdot + CO_2 + Pb^{III} \quad (11)$$

prevalent in photochemical reactions carried out in the absence of $Cu^{II}$. No doubt, higher steady-state concentrations of radicals result from photochemical (eq 11a) compared with thermal (eq 11b) initiation.[4] Furthermore, the thermal decomposition of cyclobutanecarboxylic acid (0.46 $M$) with 0.10 $M$ $Pb^{IV}$ in benzene solutions at 80° was significantly faster in the presence of catalytic amounts (0.0051 $M$) of copper(II) acetate (see Figure 1). Catalysis could be attributed to the more facile oxidation of cyclobutyl radicals by $Cu^{II}$ than by $Pb^{IV}$.[2,4] The latter is also consistent with the effectiveness of $Cu^{II}$ in reducing the amounts of cyclobutane and cyclobutylbenzene in the photochemical reactions.[15]
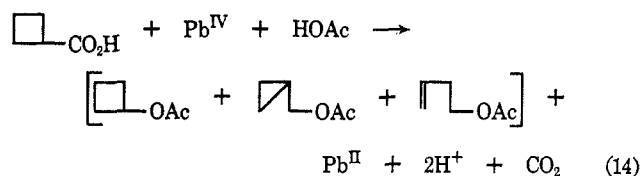
(14) Acetonitrile is a better hydrogen donor than benzene toward alkyl radicals and relatively more cyclobutane was always formed in this solvent.

Small amounts of both 1,3-butadiene and butene-1 were always found as by-products. They did not arise from isomeric impurities in the reactant acid, but were generated *via* rearrangement of cyclobutyl radicals. The latter was never a serious problem under these experimental conditions.[16,17]

$$\square\cdot \xrightarrow{\phantom{xx}} \sqcap\cdot \xrightarrow[\quad(ox)\quad]{\overset{SH}{\longrightarrow}} \begin{cases} /\!\!\!\diagup\!\!\!\diagup + S\cdot & (12) \\ /\!\!\!\diagup\!\!\!\diagup + [H\cdot] & (13) \end{cases}$$

If these minor differences are taken into account, examination of Table I shows that oxidation products from reactions carried out thermally and photochemically were equivalent.[1] In both cases decarboxylations carried out with $Cu^{II}$ in benzene solutions afforded excellent yields of cyclobutene, while in acetonitrile the most important products were a mixture of homoallylic esters. Furthermore, the composition of the mixture of rearranged homoallylic esters were invariant with the mode of initiation as well as the solvent.[18] Since the photochemical reaction could easily be carried out under mild conditions, all further studies were carried out in this manner to obviate any further rearrangements and extraneous thermal reactions.[2] The equivalence of products obtained from the photochemical and thermal decarboxylations of cyclobutanecarboxylic acid is consistent with a relatively long kinetic chain length and low activation energies in the propagation sequences (eq 1–2 and 2–4).

### Oxidative Decarboxylation of Cyclobutanecarboxylic Acid by $Pb^{IV}$. Benzene and Acetonitrile.

—Previous studies showed that pyridine enhanced the rate of decarboxylation of acids by $Pb^{IV}$ but did not affect the products.[2,4,19] The same effect was observed in the photochemical decarboxylation given in Table II. The quantum yield was not measured quantitatively, but results given in Table II show that products were also largely unaffected by changes in solvent from benzene to acetonitrile. In both solvents, a mixture of homoallylic esters[20] was the major product, together with minor amounts of cyclobutene. Slightly more

$$\square\!\!-\!CO_2H + Pb^{IV} + HOAc \longrightarrow$$
$$\left[\square\!\!-\!OAc + \diagdown\!\!\!\square\!\!-\!OAc + \sqcap\!\!-\!OAc\right] +$$
$$Pb^{II} + 2H^+ + CO_2 \quad (14)$$

(15) Part of this, however, could be due to the filtering of the irradiation by $Cu^{II}$ salts.

(16) (a) J. Roberts and R. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951); (b) E. Renk, P. Shafer, W. Graham, R. Mazur, and J. Roberts, *ibid.*, **83**, 1937 (1961); (c) C. Walling and P. Fredericks, *ibid.*, **84**, 3327 (1962); (d) L. Montgomery and J. Matt, *ibid.*, **89**, 6556 (1967).

(17) No allylcarbinyl chloride has been reported from the photochlorination of cyclobutane by chlorine[16a] or *t*-butyl hypochlorite[16c] which are effective chain-transfer agents. The Hunsdiecker reaction of silver cyclobutanecarboxylate with bromine is also reported to afford only cyclobutyl bromide.[16a] However, further facile additions may have obscured the allylcarbinyl product.

(18) The mixture of homoallylic esters could be analyzed accurately, and there was a consistent but *slight* change in composition from solvent to solvent.

(19) E. Corey and J. Casanova, *J. Amer. Chem. Soc.*, **85**, 167 (1963).

(20) The composition of the cyclobutyl derivative was always slightly greater (47%) in acetonitrile compared to benzene (42%). Other solvents show similar differences, and this has bearing on the solvation of the $C_4H_7$ cation(s). A nonclassical or three equilibrating homoallylic cations could be consistent with these observations, and we do not wish to pursue this point now.

TABLE II

EFFECT OF COPPER(II) ON THE DECARBOXYLATION OF CYCLOBUTANECARBOXYLIC ACID BY LEAD(IV) IN BENZENE AND IN ACETONITRILE[a]

| Solvent[b] (v/v) | Cu[II], M | Py, M | ▭ | ▭ | Total[c] acetates | AA | CB | CP | Total CB[c,d] carboxylates | AA | CB | CP | ▭-Ph | Sum of C4H7[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PhH (86) | 0 | 0 | 2 | 6 | 49 | (4) | (42) | (54) | 13 | (4) | (39) | (57) | 15 | 85 |
| PhH (86) | 0 | 0.060 | 2 | 5 | 41 | (4) | (42) | (54) | 11 | (4) | (39) | (57) | 12 | 71 |
| CH3CN (86) | 0 | 0 | 1 | 15 | 49 | (2) | (47) | (51) | 14 | (2) | (47) | (51) | 0[f] | 79 |
| CH2CN (86) | 0 | 0.064 | 1 | 10 | 32 | (3) | (47) | (50) | 9 | (2) | (47) | (51) | 0[f] | 52 |
| PhH (86) | 0.0051 | 0 | 68 | 1 | 12 | (5) | (42) | (53) | 4 | (10) | (41) | (49) | 2 | 87 |
| PhH (86) | 0.0051 | 0.058 | 78 | 0 | 7 | (6) | (42) | (52) | 2 | (13) | (40) | (47) | 1 | 88 |
| PhH (86) | 0.0061 | 0.0074[g] | 72 | 0.2 | 11 | (14) | (36) | (50) | 1 | N.D. | N.D. | N.D. | 1 | 85 |
| CH3CN (86) | 0.0052 | 0 | 3 | 8 | 58 | (3) | (47) | (50) | 12 | (4) | (47) | (49) | 0 | 81 |
| CH3CN (86) | 0.0055 | 0.060 | 15 | 1 | 41 | (4) | (47) | (49) | 6 | (7) | (45) | (48) | 0 | 63 |

[a] Solutions of 0.10 $M$ Pb[IV] and 0.42 $M$ cyclobutanecarboxylic acid (4% by vol.) decomposed photochemically at 30°. [b] Contains 10 parts of HOAc in addition. [c] AA = allylcarbinyl, CB = cyclobutyl, CP = cyclopropylmethyl. [d] As cyclobutanecarboxylate esters. [e] Total C4H7 fragments in products, does not include cyclobutanecarboxylate moiety. [f] Homoallylic acetamides not analyzed. [g] $\alpha,\alpha'$-Bipyridine.
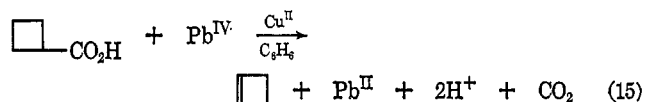
TABLE III

EFFECT OF NITRILE SOLVENTS ON DECARBOXYLATION OF CYCLOBUTANECARBOXYLIC ACID BY LEAD(IV) AND COPPER(II) [a]

| Solvent[b] (v/v) | Cu[II], M | ▭ | ▭ | Total acetates | ⌐▭-OAc | ▭-OAc | ▱-OAc | Sum of C4H7 |
|---|---|---|---|---|---|---|---|---|
| CH3CN (86) | 0.0052 | 3 | 8 | 58 | (3) | (47) | (50) | 69 |
| CH3CN (86) | 0 | 1 | 16 | 49 | (2) | (47) | (51) | 66 |
| CH3CH2CN (86) | 0.0060 | 7 | 21 | 51 | (4) | (47) | (49) | 79 |
| CH3CH2CN (86) | 0 | 4 | 34 | 38 | (3) | (47) | (50) | 76 |
| CH3(CH2)3CN (86) | 0.0060 | 18 | 13 | 38 | (4) | (47) | (49) | 69 |
| CH3(CH2)3CN (86) | 0 | 4 | 25 | 35 | (3) | (47) | (50) | 64 |
| (CH3)2CHCN (86) | 0.0059 | 10 | 26 | 36 | (4) | (47) | (49) | 72 |
| (CH3)2CHCN (86) | 0 | 4 | 29 | 25 | (4) | (45) | (51) | 58 |
| CH3CN (0.0 $M$)[c] | 0.0050 | 68 | 1[d] | 12[e] | (5) | (42) | (53) | 87 |
| CH3CN (0.81 $M$)[c] | 0.0059 | 67 | 1[d] | 14[e] | (4) | (42) | (54) | 88 |
| CH3CN (1.87 $M$)[c] | 0.0062 | 60 | 2[d] | 19[e] | (4) | (43) | (53) | 87 |

[a] Solutions of 0.10 $M$ Pb[IV] and 0.42 $M$ cyclobutanecarboxylic acid (4% by vol.) decomposed at 30° and 3500 Å. [b] In addition to 10 parts of HOAc. [c] In benzene solutions. [d] Cyclobutylbenzene (~2%) also formed. [e] Homoallylic cyclobutanecarboxylates (~4%) formed.

cyclobutane was formed in acetonitrile, probably owing to more facile hydrogen transfer from that solvent compared to benzene; this was compensated, however, by formation of reasonable amounts (12–15%) of cyclobutylbenzene.

**Oxidative Decarboxylation of Cyclobutanecarboxylic Acid by Pb[IV] in the Presence of Cu[II]. Benzene and Acetonitrile.**—A dramatic change in products with solvent was obtained when the decarboxylation of cyclobutanecarboxylic acid by Pb[IV] was carried out in the presence of catalytic amounts of copper(II) acetate (Table II). In benzene, large amounts of cyclobutene (70–80%) were formed (eq 15). In acetonitrile, ap-

$$\text{▭}-\text{CO}_2\text{H} + \text{Pb}^{IV} \xrightarrow{\text{Cu}^{II}}_{\text{C}_6\text{H}_6} \text{▭} + \text{Pb}^{II} + 2\text{H}^+ + \text{CO}_2 \quad (15)$$

proximately the same amounts of homoallylic esters as that obtained in the absence of Cu[II] were formed (eq 14). In acetonitrile, cyclobutene was a minor product which increased slightly with addition of pyridine. Cyclobutylbenzene under these conditions was no longer a significant product.

**Effect of Nitriles as Solvents for the Oxidation of Cyclobutyl Radicals by Cu[II].**—The latter two sets of experiments clearly established that it was the oxidation of cyclobutyl radicals by Cu[II] rather than Pb[IV] which

was affected by a change in solvent from benzene to acetonitrile. Acetonitrile did not affect this change in a stoichiometric manner, since relatively large amounts of acetonitrile were required before its effect was noticeable (Table III). Thus, at low concentrations of acetonitrile the behavior was indistinguishable from a reaction in benzene alone.

Homologating the alkyl chain of acetonitrile had the same effect as dilution with benzene. In the series of equivalent reactions in acetonitrile, propionitrile, valeronitrile, and isobutyronitrile as solvents, the yields of cyclobutene increased at the expense of homoallylic esters only when Cu[II] was present (Table III). Yields of cyclobutane increased directly with the hydrogen availability in the nitrile solvent; the low concentrations of Cu[II] employed in these studies were insufficient to cope completely with this side reaction.

**Effect of Solvents on the Decarboxylation of Cyclobutanecarboxylic Acid by Pb[IV].**—A variety of other solvents of different functionality was also employed (Table IV). These could be classified in several categories. (a) Hydrogen donor solvents which afforded cyclobutane in good yield. Chloroform was preeminent, followed by N,N-dimethylacetamide (DMAC) and formamide (DMF), tetrahydrofuran (THF), and hexamethylphosphoramide (HMPA). (b) Solvents in which decarboxylation of cyclobutanecarboxylic acid occurred spontaneously at room temperature. Reaction in hexamethylphosphoramide was complete in

TABLE IV

DECARBOXYLATION OF CYCLOBUTANECARBOXYLIC ACID BY LEAD(IV) AND COPPER(II) IN VARIOUS SOLVENTS[a]

| Solvent[b] | Cu$^{II}$, $M$ | Initiation[c] | □ | □ | Total acetates | ⌐—OAc | □—OAc | △—OAc | Sum of C₄H₇ |
|---|---|---|---|---|---|---|---|---|---|
| EtOAc | 0.0055 | Photo. | 77 | 2 | 11 | (4) | (42) | (54) | 90 |
| PhCl | 0.0054 | Photo. | 59 | 1 | 15 | (5) | (42) | (53) | 75 |
| CHCl₃ | 0.0055 | Photo. | 0 | 65 | 18 | (1) | (38) | (61) | 83 |
| CHCl₃ | 0 | Photo. | 0 | 64 | 19 | (1) | (39) | (60) | 83 |
| (CH₂)₄SO₂ | 0.0068 | Photo. | 24 | 5 | 46 | (3) | (47) | (50) | 75 |
| (CH₂)₄SO₂ | 0 | Photo. | 0.3 | 8 | 64 | (2) | (47) | (51) | 73 |
| DMAC | 0.0080 | R.T. | 43 | 5 | 10 | (1) | (54) | (45) | 58 |
| DMAC | 0 | R.T. | 1 | 15 | 22 | (1) | (56) | (43) | 38 |
| DMF | 0.0085 | R.T. | 34 | 10 | 15 | (2) | (56) | (42) | 59 |
| DMF | 0 | R.T. | 1 | 21 | 4 | (2) | (56) | (42) | 26 |
| Pyridine | 0.0089 | R.T. | 1 | 0.4 | ~4 | ... | ... | ... | 5 |
| Pyridine | 0 | R.T. | 0.2 | 1 | ~2 | ... | ... | ... | 3 |
| HMPA | 0.0063 | R.T.[d] | 46 | 2 | 4 | (2) | (48) | (50) | 52 |
| HMPA | 0 | R.T.[d] | 1 | 19 | 24 | (5) | (48) | (47) | 44 |
| DMSO | 0.0088 | R.T. | 34 | 2 | 7 | ... | ... | ... | 41 |
| DMSO | 0 | R.T. | 0.2 | 2 | 19 | ... | ... | ... | 23 |
| THF | 0.0088 | R.T. | 59 | 7 | 8 | (2) | (50) | (48) | 74 |
| THF | 0 | R.T. | 1 | 17 | 31 | (2) | (50) | (48) | 49 |

[a] In solutions of 0.10 $M$ Pb$^{IV}$ and 0.42 $M$ cyclobutanecarboxylic acid. [b] Solvent is 86% by vol. component listed and 10% by vol. HOAc. [c] Photo. is irradiation at 3500 Å and 30°. R.T. = initially at room temperature. Solvent added to degassed reaction mixture. [d] Exothermic.

less than 30 min. In tetrahydrofuran[21] and pyridine, decarboxylation was complete within 1 hr, and in dimethylacetamide and dimethyl sulfoxide (DMSO) the reactions took 2 and 4 hr, respectively, under the same conditions. (c) For comparison, reactions in benzene, chlorobenzene, acetonitrile, or ethyl acetate were too slow to measure at room temperature.

In all of these solvents, cyclobutene was never formed in greater than 2% yields. These results were essentially the same as the studies in benzene and acetonitrile described earlier (*vide infra*).

**Effect of Solvents on the Decarboxylation of Cyclobutanecarboxylic Acid by Pb$^{IV}$ in the Presence of Cu$^{II}$.**—Reactions examined in the previous section were repeated in the presence of catalytic amounts of Cu$^{II}$. Under these conditions, differences in the properties among solvents were again quite apparent by the relative amounts of cyclobutene and homoallylic esters produced on decarboxylation of cyclobutanecarboxylic acid. With the exception of the very active hydrogen donor solvent, chloroform, the addition of catalytic amounts of Cu$^{II}$ was sufficient to swamp the hydrogen-transfer reaction (eq 9, SH = CHCl₃), and cyclobutane in most cases was a minor product (Table IV).

According to these studies, solvents could be classified into essentially two categories, irrespective of the classification previously made in the absence of Cu$^{II}$: (i) alkene-producing, and (ii) ester-producing. In the first category (i), ethyl acetate followed by benzene, chlorobenzene, pyridine, and tetrahydrofuran appeared most effective (60-80%, cyclobutene). Other solvents such as N,N-dimethylacetamide and formamide, dimethyl sulfoxide, 1,2-dimethoxyethane, and hexamethylphosphoramide were also conducive to cyclobutene formation (35-45%). The yields of homoallylic esters in these solvents usually amounted to less than 15%. In the second category (ii) of solvents, homo-

allylic esters were the predominant product (~70%)[22a] and cyclobutene (<10%)[22b] was formed as the minor product. Acetonitrile was rather unique in this regard, although other nitrile solvents had, in degree, similar effects (Table III). Among all other non-nitrile solvents, sulfolane (tetramethylenesulfone) produced exceptional amounts of homoallylic esters. The results in chloroform were somewhat difficult to interpret owing to the overwhelming amount of cyclobutane even in the presence of Cu$^{II}$.

**Decarboxylation of Allylacetic and Cyclopropylacetic Acids.**—Essentially the same results were obtained from the decarboxylation of allylacetic acid and cyclopropylacetic acid by Pb$^{IV}$ (Table V). In every case, the products were most readily considered as arising *via* the allylcarbinyl radical. Thus, butene-1 and mixtures of homoallylic and octadienyl acetates were

$$\square\text{—CO}_2\text{H} + \text{Pb}^{IV} \longrightarrow$$

$$\square\text{.} + \text{CO}_2 + \text{Pb}^{III} + \text{H}^+ \text{ etc.} \quad (16)$$
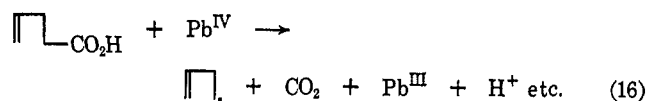
the principal products, together with allylcarbinylbenzene when the reaction was carried out in benzene. No methylcyclopropane or other derivatives (such as cyclopropylmethylbenzene) in which the cyclopropylmethyl moiety was intact could be found as products from the decarboxylation of cyclopropylacetic acid. The first-order isomerization of cyclopropylmethyl
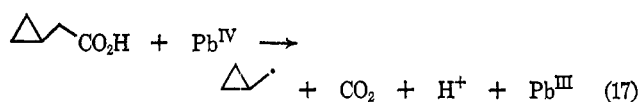
(21) Tetrahydrofuran was purified, but, since it is easily autoxidized, adventitious peroxides may have been responsible for this rate effect.²

(22) (a) There are small but reproducible changes in the distribution of homoallylic esters in various solvents.¹⁸,²⁰ The distribution in a given solvent, however, is not affected by Cu$^{II}$ (Table IV) despite large changes in total acetate yields. The solvation of C₄H₇ cation(s) appears to be independent of whether they are formed by Cu$^{II}$ or Pb$^{IV}$ oxidation (*cf.* ref 11). (b) It is interesting to note the effect of pyridine on Cu$^{II}$ oxidations in acetonitrile in promoting cyclobutene formation. The effects of pyridine and acetonitrile as ligands appear to be opposed in oxidative eliminations. Slightly better yields of cyclobutene are also obtained by addition of pyridine to the copper-catalyzed decarboxylation in benzene. It has no effect on products in the absence of Cu$^{II}$.

TABLE V

DECARBOXYLATION OF ALLYLACETIC AND CYCLOPROPYLACETIC ACIDS BY LEAD(IV) AND COPPER(II)[a]

| Acid | Solvent[b] | Cu$^{II}$, M | [radical] | [radical] | Total acetates | ⊓⌐OAc | ⊔OAc | ◁OAc | Octadienyl[c] acetates | ⊓⌐Ph |
|------|-----------|-------------|-----------|-----------|----------------|-------|------|------|------------------------|------|
| Cyclopropylacetic | CH₃CN | 0.0062 | 10 | 12 | 20 | (11) | (36) | (53) | N.D. | 0 |
| Cyclopropylacetic | CH₂CN | 0 | 25 | 0 | 10 | (8) | (32) | (60) | 0 | 0 |
| Cyclopropylacetic | PhH | 0.0064 | 1 | 38 | ~3[d] | ... | ... | ... | 20 | 1 |
| Cyclopropylacetic | PhH | 0 | 24 | 0 | 8 | (18) | (15) | (67) | 0 | 12 |
| Cyclopropylacetic | CHCl₃ | 0.0060 | 32 | 0 | N.D. | ... | ... | ... | 0 | 0 |
| Cyclopropylacetic | CHCl₃ | 0 | 11 | 0 | N.D. | ... | ... | ... | 0 | 0 |
| Allylacetic | CH₃CN | 0.0061 | 6 | 5 | 20 | (16) | (34) | (50) | 0 | 0 |
| Allylacetic | CH₃CN | 0 | 20 | 0 | ~4[d] | ... | ... | ... | 0 | 0 |
| Allylacetic | PhH | 0.0062 | 1 | 24 | ~3[d] | ... | ... | ... | 10 | 1 |
| Allylacetic | PhH | 0 | 9 | 0 | ~5[d] | ... | ... | ... | 0 | 6 |

[a] In solutions of 0.10 $M$ Pb$^{IV}$ and 0.40 carboxylic acid decomposed photochemically at 30° and 3500 Å.  [b] Solvent consists of 86% by vol. component listed and 10% by vol. HOAc.  [c] Mixture of 1-acetoxyoctadiene-2,7 and 3-acetoxyoctadiene-1,7.  [d] Estimated, ester yields too small to measure.

$$\triangle\!\!\diagup\!\!\diagdown_{CO_2H} + Pb^{IV} \longrightarrow$$

$$\triangle\!\!\diagup\cdot + CO_2 + H^+ + Pb^{III} \quad (17)$$

$$\triangle\!\!\diagup\cdot \overset{a}{\longrightarrow} \diagup\!\!\!\diagup \quad (18)$$

radicals (eq 18)[16,23] under these conditions must have been too rapid[24] compared with other second-order processes, such as hydrogen transfer, oxidation, addition, substitution, etc.

In both benzene and acetonitrile, the allylcarbinyl radicals were oxidized by Pb$^{IV}$ to a mixture of rearranged homoallylic esters in poor yields (5–10%,

$$\diagup\!\!\!\diagup\cdot + Pb^{IV} + HOAc \longrightarrow$$

$$\left[\square\!\!\!-_{OAc} + \diagdown\!\!\!-_{OAc} + \sqcap\!\!\!-_{OAc}\right] +$$
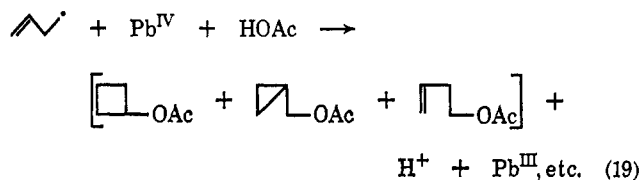
$$H^+ + Pb^{III}, etc. \quad (19)$$

Table V). The principal product was butene-1, which resulted from allylcarbinyl radicals by hydrogen abstraction (eq 20), or allylcarbinylbenzene from substitution on the solvent (eq 21). The over-all material

$$\diagup\!\!\!\diagup\cdot + SH \longrightarrow \diagup\!\!\!\diagup + S\cdot \quad (20)$$

$$\diagup\!\!\!\diagup\cdot + \bigcirc \overset{(ox)}{\longrightarrow} \diagup\!\!\!\diagup\bigcirc + [H\cdot] \quad (21)$$

balance of the C₄H₇ alkyl fragments from the decarboxylation of both acids was poor, and it may have been due to competitive decarboxylation of acetic acid since both are primary acids.[2,5]
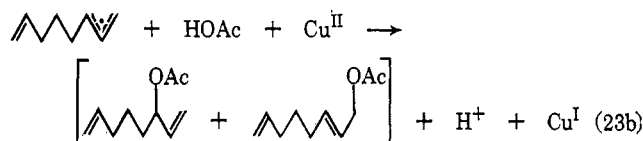
The decarboxylation of allylacetic and cyclopropylacetic acids by Pb$^{IV}$ in the presence of Cu$^{II}$ afforded two new products: 1,3-butadiene and a mixture of octadienyl acetates. A corresponding reduction in the yields of butene-1 and allylcarbinylbenzene was noted (Table V). Thus, allylcarbinyl radicals, like other primary radicals, show great selectivity toward oxidation by Pb$^{IV}$ and Cu$^{II}$.[2,5] Only the latter oxidant is capable of carrying out oxidative elimination (eq 22).[8] Other

$$\diagup\!\!\!\diagup\cdot + Cu^{II} \longrightarrow \diagup\!\!\!\diagup + H^+ + Cu^I \quad (22)$$

independent studies[25] have shown that octadienyl acetates are formed from allylcarbinyl radicals and butadiene by addition (eq 23a) followed by oxidation (eq 23b).

$$\diagup\!\!\!\diagup\cdot + \diagup\!\!\!\diagup \longrightarrow \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\cdot \quad (23a)$$

$$\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\cdot + HOAc + Cu^{II} \longrightarrow$$

$$\left[\diagup\!\!\diagdown\!\!\overset{OAc}{\diagup\!\!\diagdown} + \diagup\!\!\diagdown\!\!\diagup\!\!\overset{OAc}{\diagdown}\right] + H^+ + Cu^I \quad (23b)$$

The contrast in behavior between acetonitrile and benzene as solvents was also evident in the oxidation of allylcarbinyl radical. Thus, homoallylic esters were much more important products in acetonitrile (~20%) than they were in benzene (<3%).[26] Conversely, butadiene and octadienyl acetates were the predominant products in benzene and were less important in acetonitrile. It is significant that homoallylic esters were products even in the absence of Cu$^{II}$. It indicates that Pb$^{IV}$ was capable of oxidizing the allylcarbinyl radical to substitution products, albeit in low yield, despite its inability to effect oxidative elimination. Changes in solvent did not affect oxidative substitution of allylcarbinyl radicals by Pb$^{IV}$, similar to observations made with cyclobutyl radicals (*vide supra*).

## Discussion

The effects of solvents on the decarboxylation of cyclobutanecarboxylic, allylacetic, and cyclopropylacetic acids, in the presence and absence of Cu$^{II}$ catalyst, have furnished additional insight into the mechanism of electron-transfer oxidation of alkyl radicals by Pb$^{IV}$ and Cu$^{II}$, respectively. The products of oxidation and the enhanced rate of decarboxylation show clearly that small amounts of Cu$^{II}$ are sufficient to intercept cyclobutyl and allylcarbinyl radicals. Furthermore, hydrogen-transfer reactions in various solvents is a much more serious complication when the Cu$^{II}$ oxidant is absent. Since the rate of oxidation of alkyl radicals by Cu$^{II}$ is also close to diffusion controlled,[7] it is concluded that competition between Cu$^{II}$ and Pb$^{IV}$ for cyclobutyl or allylcarbinyl radicals

(23) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 441 ff.

(24) It is also possible that cyclopropylmethyl radicals are not intermediates and allylcarbinyl radicals are formed directly from decarboxylation (eq 17 + 18).

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

(26) The relative amounts of allylcarbinyl esters in the homoallylic mixture are greater when allylcarbinyl radicals are oxidized compared to cyclobutyl radicals. This distribution of isomers has been discussed previously.[11]

heavily favors the former under these conditions.[27a] In the following discussion, we have attributed all oxidation products[27b] derived from the copper-catalyzed decarboxylation of these acids to oxidation of the relevant alkyl radical by $Cu^{II}$ (eq 3), in preference to oxidation by $Pb^{IV}$ [28] (eq 1).

In these reactions, various amounts of reduced product (cyclobutane, butene-1) are always formed owing to differences in hydrogen donor characteristics of solvents (SH, eq 12 and 20). These products, however, will not enter further in our reckoning, since we now wish to direct our attention to a comparison of $Pb^{IV}$ and $Cu^{II}$ species as electron-transfer oxidants toward alkyl radicals.

The study of cyclobutyl radicals is particularly auspicious since competition between oxidative elimination and oxidative substitution are delicately balanced, and small perturbations in metal oxidant have large effects on the products obtained. When cyclobutanecarboxylic acid is decarboxylated by $Pb^{IV}$ in the absence of $Cu^{II}$ catalyst, the same mixture of oxidation products is obtained in a variety of solvents. In every solvent, oxidation of cyclobutyl radicals by $Pb^{IV}$ produces homoallylic esters as principal products of oxidation, and cyclobutene (*i.e.*, oxidative elimination) is always unimportant. The same is true (in degree) for the oxidation of allylcarbinyl radicals from the decarboxylation of allylacetic and cyclopropylacetic acids by $Pb^{IV}$.

*A major effect of solvent is only observed when $Cu^{II}$ is present during decarboxylation.* Thus, in most solvents $Cu^{II}$ prefers to oxidize cyclobutyl radicals by elimination to cyclobutene, despite the thermodynamic instability of the latter. It is only in acetonitrile, its homologs, and to a certain extent sulfolane that $Cu^{II}$ prefers to react with cyclobutyl radicals by oxidative substitution and affords a mixture of homoallylic esters. Under the latter circumstances, $Cu^{II}$ generates the *same mixture* of products as $Pb^{IV}$, although the rate of oxidation is much faster. The effect of solvent in affecting the course of oxidation cannot be correlated with any general bulk properties of the solvents, such as dielectric constant, ionizing power, or general polar properties (*cf.* Table IV).[29]

The unique effect of acetonitrile is attributed to specific coordination with the $Cu^{II}$ oxidant. Acetonitrile complexes of $Cu^{II}$ are known, although the formation constants are not large.[30] To obtain coordination

$$Cu^{II}(OAc)_2 + nCH_3CN \longrightarrow Cu(NCCH_3)_n(OAc)_2 \quad (24)$$
$$n = 1\text{-}6$$
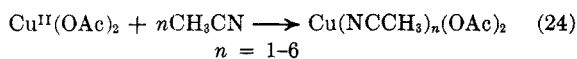
with $Cu^{II}$ (probably six), acetonitrile must be employed in large excess (solvent).[25,30a] The latter is consistent with the observations on the effects of concentration of acetonitrile and structure of nitrile-type solvents in altering oxidations by $Cu^{II}$ species (Table III).[25,31]

## Oxidative Elimination.

The formation of cyclobutene generally from reactions of cyclobutyl radicals or cyclobutyl cations (*e.g.*, from solvolysis of cyclobutyl derivatives[32]) is rather unique. Loss of a $\beta$-hydrogen atom from the radical or $\beta$ proton from the carbonium ion is never observed to a significant extent, except on oxidation of the radical by $Cu^{II}$ in non-nitrile solvents. It is concluded from this and previous studies[11] that cyclobutyl cation is not an intermediate in cyclobutene formation. Instead we associate the oxidative elim-

$$\square^{\cdot} + Cu^{II}OAc \longrightarrow \square + HOAc + Cu^{I} \quad (25)$$

ination of alkyl radicals by $Cu^{II}$ to a specific intramolecular removal of the $\beta$ hydrogen synchronously with electron transfer. Part of the driving force for such a process may be derived by synergic bonding between the incipient olefinic bond and $Cu^{I}$.[33] A transition state for oxidative elimination is represented below.[34]
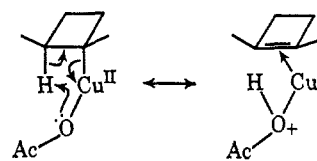


a transition state for oxidative elimination
of alkyl radicals by $Cu^{II}$ complexes

## Oxidative Substitution.

A similar process for oxidative elimination by $Pb^{IV}$ and $Cu^{II}(NCCH_3)_n$ complexes does not obtain, since little or no cyclobutene is formed. With these oxidants, a cyclobutyl cation, subject to extensive rearrangement, is an intermediate formed by electron transfer (eq 26 and 27). Oxidative substitution

$$\square^{\cdot} + Pb^{IV}O_2CR \longrightarrow C_4H_7^+ + Pb^{III}O_2CR, \text{etc.} \quad (26)$$
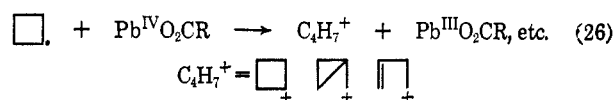
$$C_4H_7^+ = \square_+ \quad \square_+ \quad \square_+$$

*via* cations as a route to esters has been previously described.[11] A mixture of homoallylic esters is formed by rather indiscriminant solvation of the $C_4H_7$ cation(s),[35] since homoallylic acetates and cyclobutanecarboxylates are formed in direct proportion to the mole fraction of the parent acids (*cf.* Table II). Cyclobutyl, allylcar-

(27) (a) The competition is not always in favor of $Cu^{II}$, since oxidative decarboxylation of acids which yield easily oxidized radicals such as triphenylmethyl are not affected by $Cu^{II}$.[1,4] (b) Cyclobutane and butene as reduction products are not included.

(28) This is intended more for illustration rather than to point to exclusiveness, since small contributions from $Pb^{IV}$ oxidation cannot be evaluated. Internal consistency is the most important consideration.
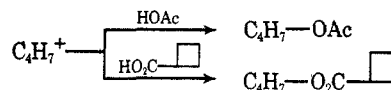
(29) A. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967).

(30) (a) C. Addison, B. Hathaway, N. Logan, and A. Walker, *J. Chem. Soc.*, 4308 (1960); (b) I. Kolthoff and J. Coetzee, *J. Amer. Chem. Soc.*, **79**, 1852 (1957).

(31) (a) In the same way, the effect of sulfolane is attributed to sulfolane complexes of $Cu^{II}$. However, it is also possible to interpret the data in Table IV as indicating that $Cu^{II}$ in sulfolane is a poor oxidant and yields cyclobutene by this route. The homoallylic esters would then be attributed to oxidation by $Pb^{IV}$. $Cu^{II}$ complexes in sulfolane are under investigation. (b) The stabilization of $Cu^{I}$ by sulfolane has not yet been reported.

(32) (a) J. Roberts and R. Mazur, *J. Amer. Chem. Soc.*, **73**, 2511 (1951); (b) K. Servis and J. Roberts, *ibid.*, **86**, 3773 (1964); **87**, 1331 (1965); *Tetrahedron Lett.*, 1369 (1967); (c) J. Roberts and R. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951); (d) R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., part 1, Interscience Publishers, New York, N. Y., 1963, p 233 ff.

(33) (a) O. Chaltykyan, "Copper-Catalytic Reactions," Consultants Bureau, New York, N. Y., 1966. (b) *Cf.* also oxidation of alkyl radicals by $Cu^{II}$.[25]

(34) Pyridine $Cu^{II}$ complexes are somewhat akin to acetato $Cu^{II}$ oxidant in that they slightly favor oxidative elimination. The basic nitrogen site may aid intramolecular proton transfer.

(35) Reaction of these $C_4H_7$ cations with acetonitrile also takes place and homoallylic acetamides are formed. This reaction, however, is not so important as it is with *t*-amyl cations.[11]

binyl, and cyclopropylmethyl derivatives comprise the isomeric esters in essentially the same proportion in each fraction. This composition varies only slightly with solvent.[20,22a]
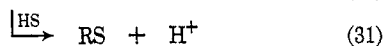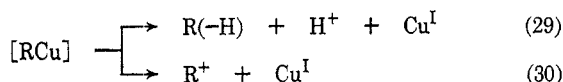
The difference between copper(II) acetate and copper(II) acetonitrile complexes as oxidants may be attributed (to a certain extent) to the higher oxidation potential of the latter. In such a case, greater driving force for electron transfer (eq 27) is derived from the

$$\square_{\cdot} \; + \; Cu^{II}(NCCH_3)_n \; \longrightarrow \; C_4H_7^+ \; + \; Cu^I(NCCH_3)_n \quad (27)$$
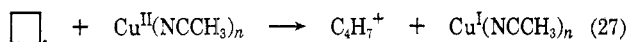
formation of the more stable acetonitrile copper(I) complex.[31b,36] In addition, competition with oxidative elimination (eq 25) is minimized by (a) displacement of the acetato ligands in the Cu[II] complex by acetonitrile, and (b) reduction of synergic bonding to alkene by the presence of acetonitrile in the copper complex[25] (*cf.* transition state for oxidative elimination).

Cyclobutyl radicals are not unique in undergoing different oxidative processes by various Cu[II] oxidants. Thus, the dichotomy between oxidative elimination and substitution has also been observed with allylcarbinyl (*vide supra*), α-phenylalkyl,[37] and 2-p-methoxyphenethyl[11] radicals. Both oxidative routes (especially cation formation, eq 30) are reasonably accessible in each of these radicals. Furthermore, the behavior of the radicals is not dependent on their mode of formation, since the same results are obtained from the copper-catalyzed decomposition of the corresponding peroxides.[11]

**Conclusions.**—Oxidative elimination and substitution are not mutually exclusive processes, but under a given set of conditions they are more often competitive. In a previous study the following mechanism[11] was proposed for the oxidation of alkyl radicals by Cu[II].

$$R_{\cdot} \; + \; Cu^{II} \; \rightleftharpoons \; [RCu] \quad (28)$$

$$[RCu] \left\{ \begin{array}{l} \longrightarrow \; R(-H) \; + \; H^+ \; + \; Cu^I \quad (29) \\ \longrightarrow \; R^+ \; + \; Cu^I \quad (30) \\ \xrightarrow{HS} \; RS \; + \; H^+ \quad (31) \end{array} \right.$$

Postulation of an alkyl copper intermediate, formed reversibly, was presented mainly on the basis of kinetic evidence. Such a metastable organocopper intermediate does not materially affect the arguments based on product studies. Equations 29 and 30 are routes *via* an organocopper species for oxidative elimination and substitution, respectively.[38,39] The former path is opti-

mum in noncomplexing solvents, and the latter reaction is aided by acetonitrile and related solvents.

On the basis of these solvent studies, an analogous mechanism is presented for the oxidation of alkyl radicals by Pb[IV]. However, with Pb[IV] as oxidant, a route

$$R_{\cdot} \; + \; Pb^{IV}O_2CR \; \rightleftharpoons \; [RPbO_2CR] \quad (32)$$

$$[RPbO_2CR] \; \longrightarrow \; R^+ \; + \; Pb^{III}O_2CR, \; etc. \quad (33)$$

for *direct* oxidative elimination similar to eq 29 for Cu[II] does not appear relevant. We consider most products as stemming from solvation, elimination, rearrangement, etc., of the intermediate alkyl cation, including alkene usually formed in minor amounts.[38b] Pb[IV] carboxylates do not appear to form complexes with acetonitrile and other ligands of the type that Cu[II] species do. Thus, the oxidation of alkyl radicals by Pb[IV] (eq 29) is singularly unaffected by solvents. The latter appear to affect only rates of decarboxylation of acids by Pb[IV], when they can exercise nucleophilic properties (*e.g.*, HMPA, DMF, DMAC, etc.) in common with observations of a variety of other bases.[2] Products of oxidation are largely unaffected by changes in solvent in these instances.

These mechanisms help to clarify the earlier observations that oxidations of alkyl radicals by Cu[II] are much more facile and less selective than analogous oxidations with Pb[IV].[2,4,7] In the former, two oxidative paths are available, one (eq 29) of which does not require direct generation of an alkyl cation. The concerted path for oxidative elimination (eq 25) enables Cu[II] to circumvent carbonium ion formation except when the latter is favorable. Those radicals (*e.g.*, neopentyl,[11] phenyl,[40] benzyl,[4,41] etc.) which neither have β hydrogens nor generate stable cationic species are oxidized only slowly by Cu[II]. On the other hand, there is one major path (eq 33) available for oxidation of alkyl radicals by Pb[IV], and it includes heterolytic dissociation (eq 33). Except for relatively stable cations (*e.g.*, *t*-alkyl, benzylic,[41] allylic, etc.) the latter is an energetically undesirable route and oxidation is generally slow.[4,11] With both Cu[II] and Pb[IV], reversible formation of the alkyl metal intermediate allows alkyl radicals to react by other homolytic processes when electron transfer is reluctant.[42]

## Experimental Section

**Materials.**—Carboxylic acids were purified by distillation and their purity confirmed by gas chromatographic (glpc) analysis of the neat acids and their methyl esters on FFAP (Varian Aerograph) and DEGS (Varian Aerograph) on firebrick. Each was shown to be free of isomeric impurities. Cyclobutanecarboxylic acid was from Columbia Organic Chemicals and allylacetic acid from Peninsular Chemical Co.

Cyclopropylacetic acid was made from ethyl vinylacetate and methylene iodide by the Simmons–Smith procedure.[43]

(36) H. Morgan, *J. Chem. Soc.*, 2901 (1923); B. Hathaway, D. Holah, and I. Postlethwaite, *ibid.*, 3215 (1961); 2444 (1962); W. Schneider and A. v. Zelewsky, *Helv. Chim. Acta*, **46**, 1848 (1963); S. Manahan and R. Iwamoto, *Inorg. Chem.*, **4**, 1409 (1965).
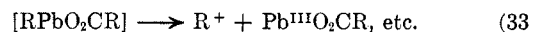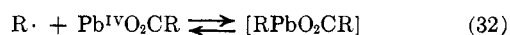
(37) Unpublished results.

(38) (a) It should be emphasized that oxidative elimination and oxidative substitution only represent *categories* of electron-transfer reactions between alkyl radicals and metal oxidant. (b) We do not mean to imply that alkenes can only be formed by the former path and esters can only be formed by the latter. Thus, it is known that carbonium ions do eliminate β protons (E1 reactions) and alkenes are often products from solvolysis and nitrosative deamination.[39] For this reason, the distinction between oxidative elimination and substitution is particularly obscured with *t*-alkyl, benzylic, and similar systems. (c) Furthermore, esters do not always arise *via* a carbonium ion since there is evidence for ligand transfer in the oxidation of allyl[9] and allylcarbinyl[11] radicals. (d) In the absence of nucleophiles such as carboxylates, etc, the carbonium ions can also react with arenes to form aromatic substitution products by electrophilic processes.

(39) C. Bunton, "Substitution Reactions," Elsevier Publishing Co., New York, N. Y., 1964; D. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963. See Y. Pocker and D. Kevill, *J. Amer. Chem. Soc.*, **87**, 4771 (1965), for recent discussions of this point.

(40) J. Kochi, *ibid.*, **79**, 2943 (1957).

(41) (a) The oxidation of benzyl radicals shows extremely large polar effects. Although benzyl radical itself is not readily oxidized, the p-methoxy isomer is. (b) *Benzylic* radicals (*i.e.*, α-phenylalkyl), which have longer side chains, are readily oxidized by virtue of being secondary radicals and also capable of oxidative elimination as well.

(42) It is not necessary to postulate an alkyllead intermediate. For example, carbonium ions can be formed directly from alkyl radicals by an outersphere electron-transfer mechanism. However, we feel that an alkyllead species is generally an intermediate[4] which reacts primarily by eq 33, although *direct* reactions on the alkyllead are also possible (J. Kochi, R. Sheldon, and S. Lande, submitted for publication).

(43) R. Smith and H. Simmons, *Org. Syn.*, **41**, 72 (1961).

Zn–Cu couple was prepared from 81 g (1.24 g-atoms) of Zn powder and 1.25 g of cupric acetate monohydrate in 125 ml of glacial acetic acid by the Le Goff procedure.[44] To this Zn–Cu couple was initially added 100 ml of anhydrous ether and 30 g of methylene iodide with stirring. This was followed by dropwise addition of a mixture of 94 g (0.83 mol) of ethyl vinylacetate and 300 g of methylene iodide (1.24 mol in all) at a rate to maintain gentle reflux. The mixture was then stirred and refluxed for 24 hr under nitrogen. Gas chromatography of the crude reaction mixture showed almost no unreacted ester, and on distillation after work-up afforded 83 g (78%) of ethyl cyclopropylacetate, bp 146–149°. The latter was hydrolyzed by stirring with a solution of aqueous methanolic potassium hydroxide at room temperature for 24 hr. Work-up and distillation yielded cyclopropylacetic acid in 70% yield, bp 86–87° (9 mm).

Lead tetraacetate (G. F. Smith Chemical Co.) was recrystallized from glacial acetic acid (containing 1–2% acetic anhydride) and vacuum desiccated over potassium hydroxide pellets. It was stored at −15° protected from light and moisture. Analysis of the white, free-flowing material by iodometric titration indicated 96–98% $Pb(OAc)_4$. Cupric acetate monohydrate (Mallinckrodt analytical reagent) and 2,2′-bipyridine (Eastman Kodak Co.) were used without further purification.

Benzene and chlorobenzene (Mallinckrodt Chemical Works) were further purified by distillation through a 22-plate Oldershaw column. Glacial acetic acid, ACS reagent (Allied Chemical Corp.) was used as supplied. Acetonitrile (Matheson reagent) was distilled from phosphorus pentoxide. Propionitrile, isobutyronitrile, valeronitrile, and benzonitrile (Eastman Organic Chemicals) and ethyl acetate and tetrahydrofuran (Du Pont Co.) were purified by distillation. Chloroform was purified[45] immediately prior to its use. Vacuum distillation of tetramethylenesulfone (Shell Development Co.) from potassium hydroxide pellets yielded crystalline, odorless material. Dimethylformamide and dimethylacetamide (Du Pont Co.), except for drying over molecular sieves, were used without further purification. Pyridine (Reilly Co.) was distilled from potassium hydroxide. Dimethyl sulfoxide and hexamethylphosphoric triamide were refluxed over calcium hydride and distilled *in vacuo*.

Authentic, characterized samples of cyclobutane and cyclobutene were generouly supplied by Dr. J. Bayless. Other $C_4$ hydrocarbons, research grade, were supplied by Phillips Petroleum Co. and J. T. Baker Chemical Co. Authentic cyclobutylbenzene, produced by photoisomerization of phenylbutadiene followed by hydrogenation, was generously donated by Dr. M. Pomerantz. Cyclopropylmethylbenzene was from Columbia Organic Chemicals Co. The preparation of 4-phenylbutene-1 has been described elsewhere.[10] *n*-Butylbenzene and *n*-butyl acetate were from Eastman Organic Chemicals.

Cyclopropylcarbinol was prepared from cyclopropanecarboxylic acid (K & K Laboratories) by reduction with lithium aluminum hydride.[46] It was isomerized to cyclobutyl alcohol[47] with hydrochloric acid. Allylcarbinol was from Aldrich Chemical Co. Each of these alcohols was esterified with acetic anhydride and cyclobutanecarbonyl chloride (Kaplop Laboratories) to prepare authentic esters.[45]

**Photolysis.**—The photolytic decarboxylations were conducted in 40 × 1 cm quartz tubes employing a Rayonet photochemical reactor (The Southern N. E. Ultraviolet Co.) Four 3500-Å lamps (3050–4150 Å) were used. The tubes were placed 10 cm from the nearest light source and the reactor temperature (30–33°) was maintained by air circulation.[1]

**Typical Procedure.**—A solution of cupric acetate monohydrate (0.0525 g, 0.253 mmol), cyclobutanecarboxylic acid (2.13 g, 21.3 mmol), glacial acetic acid (5 ml), lead tetraacetate (97%) (2.284 g, 5.00 mmol), and benzene (43 ml) was prepared with agitation in a 50-ml volumetric flask. Two 20-ml aliquots were transferred to separate tubes which were flushed free of oxygen with a stream of argon introduced *via* long stainless steel needles. The tubes were closed with rubber serum caps and placed in the photolysis chamber for 1.5 hr. The gaseous prod-

ucts were analyzed qualitatively by glpc for $CO_2$ and $C_4$ hydrocarbon, and then quantitatively for cyclobutane and cyclobutene after the introduction of *cis*-butene-2 as internal standard. The reaction mixture was transferred with glacial acetic acid to make a solution of 30-ml total volume. Aliquots of this solution were employed for further analysis. The mixture of homoallylic acetates were analyzed directly without work-up after *n*-butyl acetate was added as internal standard. The acidic nature of the solution in no way interfered with the quantitative distribution of these acetates under analytical conditions. Homoallylic acetates and cyclobutanecarboxylates, together with $C_4$ benzenes, were also determined after work-up using *n*-butyl acetate, 2-ethylhexyl acetate, and *n*-butylbenzene as internal standards. Work-up consisted of washing twice with water, dilute sodium bicarbonate, and water again and drying of the residual benzene solution over sodium sulfate.

When acetic acid was omitted from the solvent, cupric acetate was dissolved in cyclobutanecarboxylic acid and a small portion of benzene added prior to the addition of lead tetraacetate. A heterogeneous system resulted otherwise, with most of the $Cu^{II}$ salt precipitating.

When pyridine was part of the system, it was added to a mixture of cupric acetate and the carboxylic acid (or directly to the carboxylic acid in those runs without $Cu^{II}$) prior to the addition of lead tetraacetate. Similarly, the $\alpha,\alpha'$-bipyridine $Cu^{II}$ complex was initially prepared in the carboxylic acid prior to the addition of lead tetraacetate.

**Thermolysis.**—The thermal (81°) decarboxylations in benzene, chlorobenzene, and acetonitrile were conducted in an oxygen-free system as described earlier.[2] Solutions for these reactions were prepared in volumetric flasks and transferred to the reaction vessel as described above for photolysis.

Decarboxylations using dimethylformamide (DMF), dimethylacetamide (DMAC), hexamethylphosphoramide (HMPA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), or pyridine as solvents were conducted as follows. Cupric acetate (0.0239 g, 0.120 mmol) was dissolved in cyclobutanecarboxylic acid (0.674 g, 6.74 mmol) in a 125-ml erlenmeyer flask. Lead tetraacetate (97%) (0.689 g, 1.51 mmol) and glacial acetic acid (1.5 ml) were added, and the vessel was capped with a rubber septum. The solution and vessel were flushed with argon and 13 ml of DMAC previously flushed with argon was added with a syringe. Some heat was evolved upon mixing. The resulting homogeneous solution was stirred in the dark at 28 ± 1° for 2 hr. Product analysis was then carried out as above.

**Analytical Procedures.**—Reaction mixtures were analyzed by quantitative gas chromatography (glpc) using various internal standards (*vide supra*) which were previously calibrated against individual reaction products. Identification of gas chromatographic peaks was verified by comparing their retention times with authentic compounds on at least two columns of different polarity. Identification was confirmed by chemical degradation of reaction products (*e.g.*, hydrogenation of olefins and hydrolysis of esters) and comparison of degradation products with authentic samples by glpc.

Gas chromatographic analysis of gaseous hydrocarbons was performed on Case-constructed instruments equipped with thermal conductivity detectors. A 15 ft × 0.25 in. 30% Dowtherm A on firebrick column at 25° was employed for $C_4$ hydrocarbon analyses.

Other analyses were performed on an Aerograph HiFy (Model 600D) instrument equipped with a flame ionization detector. A 6 ft × 0.125 in. 20% FFAP on acid-washed Chromosorb W column was employed at 85° for acetate analyses and at 150° for the cyclobutanecarboxylates and alkylbenzene analyses.

(44) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(45) A. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p 176.

(46) J. Roberts and R. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

(47) M. Caserio, W. Graham, and J. Roberts, *Tetrahedron*, **11**, 171 (1960).