Oxidative Cleavage of Cyclopropanes. VI. Kinetics of the Cleavage of Arylcyclopropanes by Lead Tetraacetate[1,2]

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Abstract: Six arylcyclopropanes have been cleaved by lead tetraacetate. The reaction is over-all second order, first order in each reactant. A correlation of the second-order rate constants and σ^+ has been observed for the substituents p-CH_3O, p-CH_3, m-CH_3, H, p-Cl, and m-Cl at 75.8° with $\rho^+ = -1.75$. Activation parameters for the reaction have been determined from the rates of the reactions at 25.0, 50.1, and 75.8°. The products of the reaction are cinnamyl acetates and 1-aryl-1,3-propanediol diacetates. No cleavage of the alternate cyclopropane bond occurs. The addition of perchloric acid markedly enhances the rate of cleavage of phenylcyclopropane by the lead(IV) species in solution. An equilibrium exists between lead tetraacetate and perchloric acid yielding $Pb(OAc)_3^+ClO_4^-$, which is the reacting electrophile. The equilibrium constant for the formation of the ion pair in acetic acid at 25° is 23.7 l. mol^{-1}. Comparative rate studies of the cleavage of p-methylphenylcyclopropane, phenylcyclopropane, and m-chlorophenylcyclopropane by $Pb(OAc)_3^+ClO_4^-$ indicates that while its reactivity parallels that observed for $Pb(OAc)_4$ the $\rho^+ = -1.3$ suggests that the reaction of $Pb(OAc)_4$ does not proceed *via* $Pb(OAc)_3^+$-OAc^-. Support for this conclusion is provided by equilibrium studies. The cleavage reaction with $Pb(OAc)_4$ is postulated to proceed *via* a concerted mechanism in which the cyclopropane ring becomes coordinated with lead as an acetate ion leaves.

While lead tetraacetate has distinguished itself as a versatile and powerful reagent in the field of organic chemistry for nearly 50 years, the mechanisms of its reaction have remained largely an enigma except for the cleavage of diols.[4] The mode of reaction is strongly dependent on the substrate and the reaction conditions. There have been numerous product studies of oxidative processes involving lead tetraacetate which unfortunately have provided little insight into the nature of the reacting species. Many of the product studies are lacking in terms of modern techniques. In spite of the possibility of undetected reaction products, the mechanisms of reaction and the exact nature of the attacking species have been widely discussed.[4] Among the many active intermediates postulated, $Pb(OAc)_3^+$ has received the most attention.

The $Pb(OAc)_3^+$ moiety is assumed to behave as an electrophile and results in the formation of organolead compounds, which in subsequent steps lose $Pb(OAc)_3^-$. In contrast to the vast body of information available on reaction products, kinetic data are sparse. While product studies lend themselves to consistent models for the molecular transformation of the postulated attacking species $Pb(OAc)_3^+$, there is a need for examining many known reactions of lead tetraacetate in kinetic terms.

Our previous work on the kinetics of cleavage of arylcyclopropanes by coordinatively unsaturated mercuric acetate[5] and thallium triacetate[1] was designed to provide some basis for the study of a broad spectrum of electrophilic attacking species. A study of the corresponding reaction with the coordinatively saturated lead tetraacetate is a logical extension in a series of closely related electrophilic reagents as lead tetraacetate often has been compared to mercuric acetate in its reactions. However, thallium triacetate should be more closely related to lead tetraacetate in a periodic sense. Furthermore the renowned but ill-defined $Pb(OAc)_3^+$ is isoelectronic with $Tl(OAc)_3$. We now report the kinetics of the cleavage of substituted phenylcyclopropanes by lead tetraacetate in an attempt to provide a comparison of the electrophilicities of a series of periodically related metal acetates.

Results

Product Analysis. Substituted phenylcyclopropanes were cleaved with lead tetraacetate in anhydrous acetic acid at 75° using 50% excess cyclopropane. The mode of analysis for the only two products detected, cinnamyl acetates and 1-aryl-1,3-propanediol diacetates,[6,7] was the same as that described before.

Stability of Lead Tetraacetate. The previously observed instability of mercuric acetate and thallium triacetate in acetic acid prompted us to examine the stability of lead tetraacetate. Lead tetraacetate solutions in acetic acid decrease in their oxidative titer. No complete kinetic analysis was undertaken as it was felt to be sufficient to determine the limitation that the decomposition imposed on our studies of the cleavage of cyclopropanes. The calculated rate constant for an

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[1] Paper V: A. South, Jr., and R. J. Ouellette, *J. Am. Chem. Soc.*, **90**, 7064 (1968).

[2] This research was supported by Grant GP6778 from the National Science Foundation.

[3] National Science Foundation Undergraduate Research Participant.

[4] R. Criegee, "Oxidation in Organic Chemistry," Vol. 5-A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 5.

[5] R. J. Ouellette, R. D. Robins, and A. South, Jr., *J. Am. Chem. Soc.*, **90**, 1619 (1968).

[6] We reported the presence of a small quantity of 2-phenyl-1,3-propanediol diacetate in the vpc collected diacetate fraction of the reaction mixture.[7] At that time we were unable to separate the isomeric diacetates and relied on the nmr of the diacetate fraction. Conditions have been found for the separation of the isomers and there is no detectable amount of the previously reported product. There is a possibility that 1-phenyl-1,3-propanediol diacetate pyrolyzed to a small degree in our vpc collection procedure. The methylene protons of cinnamyl acetate exhibit a doublet at the same field position as the methylene protons in 2-phenyl-1,3-propanediol diacetate.

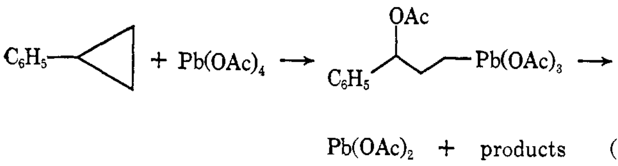
[7] R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 1651 (1964).

Table I. Cleavage Products of Arylcyclopropanes by Lead Tetraacetate

Substituent	Cinnamyl acetate, % yield Vpc	Nmr	1-Aryl-1,3-propanediol diacetate, % yield Vpc	Nmr
p-CH$_3$O	20	. .	80	. .
p-CH$_3$	22	. .	78	. .
m-CH$_3$	27	23	73	77
H	29	. .	71	. .
p-Cl	26	22	74	78
m-Cl	21	16	79	84

assumed first-order reaction is 3.7×10^{-4} min^{-1} for an initial concentration of 0.021 M at 76°. With the addition of sufficient perchloric acid to produce a 0.15 M solution the rate of decomposition of lead tetraacetate is greatly accelerated. A 10% change in the oxidative titer occurs in 30 min at 25°. The rate of cleavage of cyclopropanes by lead tetraacetate is much slower than the two metal acetates previously examined. This fact dictated the use of excess concentrations of the cyclopropanes in order to study the cleavage reaction.

Kinetic Analysis of Cleavage by Pb(OAc)$_4$. All attempts to isolate and characterize lead tetraacetate adducts of olefins have failed except in one case in which a nonsolvolytic medium was used.[8] Therefore it was anticipated that there would be no significant buildup of oxyplumbated intermediate and that the rate of cleavage could be monitored by the change in the oxidative titer of the reaction mixture.



(1)

Analysis of the lead(IV) content of the solutions was accomplished by the addition of excess aqueous potassium iodide to aliquots of the reaction mixture. The resulting triiodide generated was titrated with standard sodium thiosulfate in the presence of a starch indicator. The end point was a yellow heterogeneous mixture of lead diiodide.

The rate of decomposition of lead tetraacetate constitutes a problem in kinetic analysis of the rate of cleavage of cyclopropanes. Only in the case of p-methoxyphenylcyclopropane could equimolar concentrations of cyclopropane and lead tetraacetate be used. In all other cases, a three- to tenfold excess of the cyclopropanes was necessary in order to speed the rate of cleavage relative to the rate of decomposition. As the electron-withdrawing nature of the ring substituent increased, the concentration of the cyclopropane had to be increased.

The kinetic order of the cleavage of cyclopropanes by lead tetraacetate is two. An integrated rate expression which was used to fit the data is given in eq 2. The

$$\log \frac{(A_0 - x)B_0}{(B_0 - x)A_0} = \frac{k(A_0 - B_0)t}{2.303} \tag{2}$$

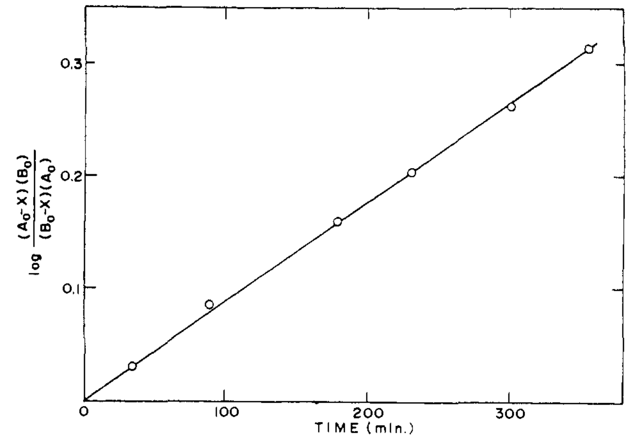


Figure 1. Second-order kinetic plot for the cleavage of p-methylphenylcyclopropane by Pb(OAc)$_4$ in acetic acid at 50.1°

terms A_0 and B_0 refer to the initial concentrations of cyclopropane and lead tetraacetate, respectively. Therefore, $B_0 - x$ is the observed titer of the lead(IV) solution and the term $A_0 - x$ is evaluated on the basis of a 1:1 stoichiometric reaction between the cyclopropane compound and lead tetraacetate. A typical kinetic plot for the cleavage of p-methylphenylcyclopropane (0.0208 M) at 50.1° is shown in Figure 1.

All rates of cleavage were slow enough to allow ready sampling using conventional volumetric techniques. The concentrations of cyclopropanes and the times chosen to terminate analysis were dictated by the limitation of the decomposition of lead tetraacetate. In no case was the reaction followed beyond a point where 5% decomposition of lead tetraacetate could occur. The initial concentration of lead tetraacetate was maintained at *ca.* 0.02 M while the cyclopropane concentrations varied from 0.02 to 0.2 M. The observed rate constants as a function of substituent and temperature are listed in Table II.

Table II. Rates of Cleavage by Pb(OAc)$_4$

Substituent	T, °C	k, l. mol^{-1} min^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg
p-CH$_3$O	75.8	4.9×10^{-1}		
p-CH$_3$	75.8	1.08×10^{-1}		
p-CH$_3$	50.1	1.09×10^{-2}	19.2 ± 0.3	−16.4 ± 1.0
p-CH$_3$	25.0	8.2×10^{-4}		
m-CH$_3$	75.8	4.5×10^{-2}		
H	75.8	2.8×10^{-2}		
H	50.1	2.8×10^{-3}	19.6 ± 0.3	−17.8 ± 1.0
H	25.0	2.0×10^{-4}		
p-Cl	75.8	1.8×10^{-2}		
m-Cl	75.8	5.7×10^{-3}		
m-Cl	25.0	3.8×10^{-5}	19.8 ± 0.3	−20.4 ± 1.0

There is no detectable effect on the rate of the reaction as lead diacetate accumulates. Furthermore the addition of lithium acetate does not affect the rate of cleavage. For an equimolar amount of lithium acetate as compared to lead tetraacetate $k = 1.07 \times 10^{-1}$ l. mol min at 75.8° for p-methylphenylcyclopropane. This value is within experimental error of the rate constant in the absence of lithium acetate.[9]

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(8) K. C. Pande and S. Winstein, *Tetrahedron Letters*, 3393 (1964).

(9) This observation provides a dramatic contrast to thallium triacetate in which thallous acetate drastically inhibits the reaction. See ref 1.

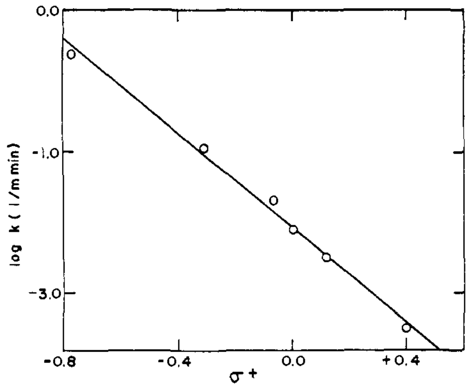

Figure 2. Hammett correlation of rates of cleavage by $Pb(OAc)_4$ with σ^+.

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ listed in Table II were calculated from a plot of $\ln k/T$ *vs.* $1/T$. The reported limits of error represent a reasonable estimate on the basis of an assumed accuracy of 5% in the rate constants and consideration of the temperature range employed.[10] The entropies of activation are calculated at 50.1°.

A Hammett plot for the rate constants at 75.8° is shown in Figure 2. The calculated response of rate to the change in substituent is given by $\rho^+ = -1.75$ with a correlation coefficient of 0.99.

Reaction of $Pb(OAc)_4$ with $HClO_4$. The basicity of $Pb(OAc)_4$ toward perchloric acid was determined in acetic acid containing sufficient acetic anhydride to react with the water contained in the perchloric acid. The visible spectral studies at 25° were similar to those reported by Lemaire.[11] The value for the equilibrium constant, $K_f^{\mathrm{BHClO_4}}$, for the reaction of the base 2-chloro-4-nitroaniline with perchloric acid was determined as 2.4×10^{-4} l./mol. The difference between this value and that reported by Lemaire (1.22×10^{-3} l./mol) may reflect a difference in the acetic acid solvent.

Lead tetraacetate reacts with perchloric acid to form $Pb(OAc)_3^+ClO_4^-$ in a manner similar to that reported for the reaction of $Hg(OAc)_2$ with perchloric acid.[12] The equilibrium constants for the reaction of $Hg(OAc)_2$, $Pb(OAc)_4$, and $Pb(OAc)_2$ were determined as 23.5, 23.7, and 246 l./mol, respectively, at 25°.

$$\mathrm{Hg(OAc)_2 + HClO_4} \xrightleftharpoons{K_f^{\mathrm{HgOAc^+ClO_4^-}}} \mathrm{HgOAc^+ClO_4^-} \tag{3}$$

$$\mathrm{Pb(OAc)_4 + HClO_4} \xrightleftharpoons{K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}} \mathrm{Pb(OAc)_3{}^+ClO_4^-} \tag{4}$$

$$\mathrm{Pb(OAc)_2 + HClO_4} \xrightleftharpoons{K_f^{\mathrm{PbOAc^+ClO_4^-}}} \mathrm{Pb(OAc)^+ClO_4^-} \tag{5}$$

Cleavage Reaction with $Pb(OAc)_3^+ClO_4^-$. The rapid rate of decomposition of the ion pair, $Pb(OAc)_3^+$ ClO_4^-, in acetic acid at 25° necessitated the use of excess concentrations of the cyclopropane compounds. In order to follow the rapid change in oxidative titer of the Pb(IV) solutions a partitioned flask was employed.[1] Each single point run was quenched with KI solution and the total lead(IV) concentration was determined by titration of the iodine generated.

The rate of disappearance of all Pb(IV) species as indicated by the change in the oxidative titer of the solution is given in differential form in eq 6. Since

$$\frac{-\mathrm{d}\Sigma\mathrm{Pb(IV)}}{\mathrm{d}t} = k^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}[\mathrm{C_6H_5\text{-}}c\mathrm{\text{-}C_3H_5}][\mathrm{Pb(OAc)_3{}^+ClO_4^-}] \tag{6}$$

ΣPb(IV) is equal to the sum of $[Pb(OAc)_4]$ and $[Pb(OAc)_3^+ClO_4^-]$, and $K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}$, the equilibrium constant, is known, eq 6 may be transformed into eq 7 by substituting in the proper identities.

$$\frac{-\mathrm{d}\Sigma\mathrm{Pb(IV)}}{\mathrm{d}t} = k^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} \times [\mathrm{C_6H_5\text{-}}c\mathrm{\text{-}C_3H_5}][\Sigma\mathrm{Pb(IV)}] \times \frac{[\mathrm{HClO_4}]}{1 + K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}[\mathrm{HClO_4}]} \tag{7}$$

The concentration of $HClO_4$ is a variable during the course of the reaction as it reacts with both $Pb(OAc)_4$ and $Pb(OAc)_2$. In order to integrate eq 7, the concentration of $HClO_4$ must be expressed in terms of ΣPb(IV). Accordingly the free-acid concentration was calculated as a function of ΣPb(IV) during the course of the reaction from $K_f^{\mathrm{Pb(OAc)^+ClO_4^-}}$ and $K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}$, the known equilibrium constants. A working curve of the relationship between $HClO_4$ and ΣPb(IV) is given in Figure 3 for initial formal concentrations of 0.024 and 0.37 for $Pb(OAc)_4$ and $HClO_4$, respectively. From such nearly linear relationships, equations of the form $\mathrm{HClO_4} = b\Sigma\mathrm{Pb(IV)} + c$ were calculated.[13] Substitution of this generalized equation into eq 7 yields eq 8 in which a is the initial concentration of phenylcyclopropane and d is equal to $1 + cK_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}$.

$$\frac{-\mathrm{d}\Sigma\mathrm{Pb(IV)}}{\mathrm{d}t} = k^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} K^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} \times \frac{(a - x)(x)(bx + c)}{K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} bx + d} \tag{8}$$

The integrated form of eq 8 is given in eq 9.

$$\frac{bK_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}}{ab + c} \log\left(\frac{a - x}{bx + c}\right) + \frac{d}{a^2b + ac}\log(a - x) + \frac{bd}{abc + c^2} \times \log(c + bx) - \frac{d}{ac}\log x = \frac{k^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}} K_f^{\mathrm{Pb(OAc)_3{}^+ClO_4^-}}}{2.303} t + \text{constant} \tag{9}$$

The rate constants for the cleavage of the cyclopropanes by $Pb(OAc)_3^+$ ClO_4^- at 25° are given in Table III. For the compounds investigated the Hammett relationship with σ^+ gives $\rho^+ = -1.3$.

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[10] J. E. Leffler, *J. Org. Chem.*, 31, 533 (1966).

[11] H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, 73, 5198 (1951).

[12] A. J. Kresge, M. Dubeck, and H. C. Brown, *J. Org. Chem.*, 32, 745 (1967).

[13] We wish to thank Professor Jack Hine for his suggested treatment of the kinetic expression.

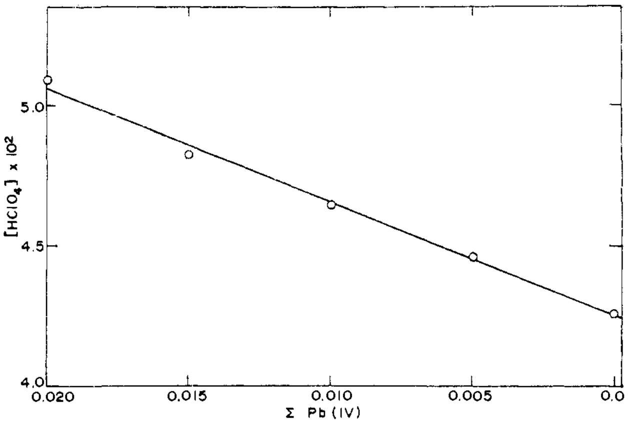

Figure 3. Calculated working curve for determining the concentration of $HClO_4$ as a function of ΣPb.

Table III. Rate of Cleavage of Arylcyclopropanes by $Pb(OAc)_3{}^+ClO_4{}^-$ at 25°

Substituent	Concn, M	[HClO$_4$]	k_+, l. mol^{-1} min^{-1}
p-CH$_3$	0.1737	0.061	1.15
H	0.2211	0.061	0.47
H	0.1276	0.061	0.49
H	0.2461	0.097	0.58
H	0.1068	0.097	0.64
m-Cl	0.3200	0.061	0.14

Discussion

The second-order rate constants for the cleavage of phenylcyclopropane by mercuric acetate, thallium triacetate, and lead tetraacetate at 25° are 1.7×10^{-4}, 2.0×10^{-3}, and 3.1×10^{-6} l. (mol sec)$^{-1}$, respectively, corresponding to relative rates of 1, 12, and 0.018, respectively. Therefore, mercuric acetate and thallium triacetate appear to be somewhat similar in terms of their relative electrophilicities, whereas lead tetraacetate reacts at a slower rate. On the basis of either oxidation state or nuclear charge the electrophilicity of lead tetraacetate would be expected to be greater than that of thallium triacetate. However, there are important structural considerations. Lead tetraacetate is coordinatively saturated and would have to lose an acetate ion simultaneously with the incorporation of the cyclopropane in a coordinate position. The required loss of the acetate ion should decrease the electrophilicity of lead tetraacetate.

Species other than the covalent compounds also must be considered as the active reagent. For $Pb(OAc)_4$ one or more related free ions may result from the ionization of acetate ions. However, in acetic acid their concentration should be quite low. Furthermore, the absence of a common ion effect with added lithium acetate indicates that free ions such as $Pb(OAc)_3{}^+$ are not kinetically important species.

It could be argued that ion-paired metal cations are important contributors to the cleavage reaction. Neglecting coordinated solvent molecules for the sake of clarity, a general kinetic scheme such as that depicted below is consistent with the experimental facts available. The apparent rate constant would be k_+K_i if the ion pair were the sole reacting species. Interpretation of the

$$M(OAc)_x \overset{K_i^{M(OAc)_x}}{\rightleftharpoons} M(OAc)_{x-1}{}^+OAc^-$$

$$M(OAc)_{x-1}{}^+\ OAc^- + C_6H_5\text{-}c\text{-}C_3H_5 \xrightarrow{k_+} \text{products}$$

$$M(OAc)_x + C_6H_5\text{-}c\text{-}C_3H_5 \xrightarrow{k_0} \text{products}$$

rates of cleavage of cyclopropanes would be complicated by changes in both K_i and k_+ if this mechanism prevailed in all of the metal acetates studied. However, in the case of both mercuric acetate and thallium triacetate we found no compelling reason for utilizing ion-paired electrophiles as the compounds are coordinatively unsaturated. Arguments for the reaction of covalent compounds have been presented.[1,5] The data presented in this paper will further support these conclusions.

If lead tetraacetate reacts as $Pb(OAc)_3{}^+OAc^-$, then the observed response of rates of cleavage to changes in ring substituents should be nearly identical with that for $Pb(OAc)_3{}^+ClO_4{}^-$. This approximation parallels that of Kresge[14] in which he assumed that the rates of reaction of $Hg(OAc)^+OAc^-$ and $Hg(OAc)^+ClO_4{}^-$ with aromatic compounds are nearly equal. The ρ^+ values for the cleavage reaction by $Pb(OAc)_4$ and $Pb(OAc)_3{}^+ClO_4{}^-$ at 26° are −1.9 and −1.3, respectively, and suggest that $Pb(OAc)_4$ does not react *via* $Pb(OAc)_3{}^+OAc^-$.

It could be argued that the observed ρ^+ values for $Pb(OAc)_4$ and $Pb(OAc)_3{}^+ClO_4{}^-$ reactions are consistent with the intermediacy of $Pb(OAc)_3{}^+OAc^-$ which reacts in a more discriminate manner than $Pb(OAc)_3{}^+ClO_4{}^-$. In the absence of additional information this possibility would have to be considered probable. If the reaction of $Pb(OAc)_4$ does proceed by way of $Pb(OAc)_3{}^+OAc^-$, then the observed rate constant must be equal to the product of the $K_i{}^{Pb(OAc)_3{}^+OAc^-}$ and a second-order rate constant $k_+{}^{Pb(OAc)_3{}^+OAc^-}$. The best estimate of the necessary second-order rate constant is that it is equal to $k^{Pb(OAc)_3{}^+ClO_4{}^-}$. Therefore, the value of the ion-pair formation constant must be approximately 10^{-4} if the reaction does proceed *via* the ion-paired species.

Kresge calculated $K_i{}^{Hg(OAc)^+OAc^-} = 2 \times 10^{-8}$ from an equation given by Bruckenstein.[14] Three known equilibrium constants were used in the calculation and it was assumed that the two unknown equilibrium constants are equal and cancel from the expression. *A priori* the equilibrium constant for ion-pair formation of $Pb(OAc)_4$ would be expected to be less than that for $Hg(OAc)_2$. This prediction is based on the larger charge and smaller ion size of Pb^{4+} as compared to Hg^{2+}. The equilibrium constants for the reactions given in eq 3 and 4 are available from our studies. The equilibrium constant of 1.0 for the reaction given in eq 10 indicates that

$$Hg(OAc)^+ClO_4{}^- + Pb(OAc)_4 \rightleftharpoons Hg(OAc)_2 + Pb(OAc)_3{}^+ClO_4{}^- \quad (10)$$

the presence of three acetate ligands in $Pb(OAc)_3{}^+ClO_4{}^-$ as compared to one ligand in $Hg(OAc)^+OAc^-$ must serve to balance the differences in ion size and charge. The equilibrium constant reflects the nearly identical behavior of the metals in the ionization of an acetate ion and association with a perchlorate ion. Therefore, the K_i values for $Hg(OAc)_2$ and $Pb(OAc)_4$ must be iden-

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(14) S. Bruckenstein in "Treatise on Analytical Chemistry," Vol. I, Part I, I. M. Kolthoff and P. J. Elving, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959.

tical. The value calculated by Kresge is 10^4 smaller than that calculated for this work assuming that the cleavage reaction of $Pb(OAc)_4$ proceeds *via* the ion pair $Pb(OAc)_3^+OAc^-$. Therefore the available data of both the ρ^+ values and the unreasonable K_i value for $Pb(OAc)_4$ suggest that ion-pair formation does not occur prior to cleavage of the cyclopropane ring. The ion-pair cleavage reaction can be calculated to be 10^{-4} slower than the observed reaction rate.

The cleavage of arylcyclopropanes by lead tetraacetate must proceed *via* the covalent $Pb(OAc)_4$ which serves as the electrophile. The reaction must involve a concerted pathway similar to an S_N2 displacement mechanism in which the cyclopropane ring electrons replace an acetate ion from the coordination sphere of Pb(IV).

The slower rate of cleavage by $Pb(OAc)_4$ as compared to $Hg(OAc)_2$ and $Tl(OAc)_3$ must reflect the difference in the ligand displaced from the coordination sphere by the cyclopropane ring. In the case of the coordinatively unsaturated compounds the ligand replaced is probably a solvent molecule which should be displaced more readily than an acetate ion.

The selectivity of lead tetraacetate as reflected by ρ^+ is significantly lower than both the selectivity of $Hg(OAc)_2$ and $Tl(OAc)_3$. Thus the reactivity–selectivity relationship appears to be reversed for $Pb(OAc)_4$, which is both the least reactive and least selective of the metal acetates. However, the reactivity–selectivity relationship does not apply if there are differences in the mechanisms of the reactions. The reaction of lead tetraacetate with its loss of acetate by displacement may in fact be more of a concerted process in which the departing acetate ion becomes attached to the developing carbonium ion center at the benzylic carbon. Therefore, the reaction of lead tetraacetate might be regarded as having a degree of concerted addition reaction character whereas the sequence of steps for mercuric acetate and thallium triacetate, which are more effective electrophiles, allow the generation of a greater positive charge at the benzylic carbon. The acetate ligands remain more strongly bonded to the metal in the case of mercury and thallium as compared to lead.

Experimental Section

Purification of Lead Tetraacetate. Approximately 25 g of lead tetraacetate was recrystallized under a nitrogen atmosphere from 500 ml of acetic acid containing 20 ml of acetic anhydride. The solution was cooled gradually over a 12-hr period to room temperature. The white crystals were filtered under the inert atmosphere and then quickly transferred to a container in a bell jar. The bell jar was evacuated to 0.2 mm for 20 hr. After drying the sample was maintained in a vacuum dissicator. With reasonable care the formation of the brown oxide that results from hydrolysis can be avoided.

Analysis of Lead Tetraacetate. The purity of lead tetraacetate was determined by weighing approximately 0.2 g in a flask containing 25 ml of acetic acid. Aliquots of 5 ml were then pipetted into 15 ml of a 5% potassium iodide solution. In the presence of a starch indicator the heterogeneous mixture was green. The sample was then titrated to a heterogeneous yellow mixture using a standard sodium thiosulfate solution. The purity of lead tetraacetate samples was in excess of 95%.

Kinetic Analysis. All runs were made by mixing standardized solutions of lead tetraacetate with a solution of the arylcyclopropane. Except in the case of *p*-methoxyphenylcyclopropane, excess cyclopropane was used. The concentration of lead tetraacetate was maintained at 0.2 *M*. For the run at 76°, 4-ml aliquots were sealed in test tubes. At 50° the aliquots were removed directly from a flask maintained at constant temperature. The lead tetraacetate titer was determined using the iodide method outlined above.

Product Analysis. The products were analyzed by the same procedure outlined in the previous paper.[1]

Determination of Equilibrium Constants. The molar extinction coefficient of 4-chloro-2-nitroaniline at 410 mμ is 4470. The optical density of a solution containing 3.7×10^{-4} *M* indicator and 2.44×10^{-5} *M* perchloric acid is 0.166 corresponding to a calculated K_a for the indicator of 2.36×10^{-4} l./mol. For formal concentrations of 3.7×10^{-4}, 5.0×10^{-2}, and 2.44×10^{-3} for the indicator, mercuric acetate and perchloric acid, respectively, the observed OD is 0.32 corresponding to a $K_f^{Hg(OAc)^+ClO_4^-} = 23.7$ l./mol. For formal concentrations of 3.7×10^{-4}, 1.23×10^{-3}, and 2.44×10^{-3} for the indicator lead diacetate and perchloric acid, respectively, the OD is 0.20 corresponding to $K_f^{Pb(OAc)^+ClO_4^-} = 246$ l./mol. For formal concentrations of 3.7×10^{-4}, 2.72×10^{-2}, and 2.44×10^{-3} for the indicator, lead tetraacetate and perchloric acid, respectively, the OD is 0.25 corresponding to $K_f^{Pb(OAc)_3^+ClO_4^-} = 23.7$ l./mol.

Cleavage Reaction with $Pb(OAc)_4$ Containing $HClO_4$. A stock solution of perchloric acid was made up gravimetrically in purified acetic acid. The perchloric acid employed was 70% by weight. A calculated quantity of acetic anhydride was added to ensure that all of the water was removed. The stock solution of lead tetraacetate was prepared gravimetrically. The desired quantity of arylcyclopropane was weighed out and transferred into a vessel containing the lead tetraacetate solution. Aliquots of the resulting solution and of the perchloric acid solution were placed in separate compartments of a partitioned flask. After equilibration the contents were mixed over the partition barrier and the lead(IV) titer change was determined after a specified period of time had elapsed. The lead(IV) initial concentration was approximately 0.02 *M* in all cases. The cyclopropane concentrations varied from a 1.5- to a 16-fold excess depending upon the concentration of perchloric acid and the structure of the substrate employed.