Oxidative Cleavage of Cyclopropanes. V. The Kinetics of the Cleavage of Arylcyclopropanes by Thallium Triacetate[1,2]

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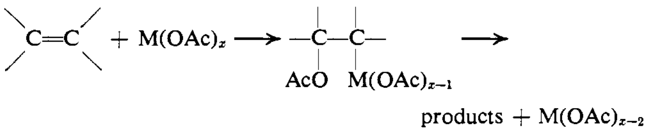
Abstract: The cleavage of six arylcyclopropanes by thallium triacetate in acetic acid has been studied. Only one of the two nonequivalent cyclopropane ring bonds is cleaved. The products of the reaction are substituted cinnamyl acetates and 1-aryl-1,3-propanediol diacetates which are postulated to be derived from intermediate organothallium adducts of the cyclopropane ring which then decompose under the reaction conditions. The kinetics of cleavage of six arylcyclopropanes have been determined and the reaction is over-all second order, first order in each reactant. Activation parameters have been determined from the rates of cleavage of phenylcyclopropane at 29.6, 50.1, and 76.2°. Electron-releasing groups facilitate the reaction and a correlation with σ^+ has been observed with $\rho = -4.3$ at 50° for the substituents p-CH_3O, p-CH_3, m-CH_3, H, p-Cl, and m-Cl. Thallium triacetate is postulated to electrophilically attack the cyclopropane bond without prior ionization. The reactivity and selectivity of thallium triacetate are compared with mercuric acetate. Determination of the kinetics of the reaction is complicated by double salt formation between $Tl(OAc)_3$ and TlOAc. An equilibrium exists between these two salts under the reaction conditions, and $Tl_2(OAc)_4$ has been isolated. The double salt is a much weaker electrophile than thallium triacetate, and cleavage with it occurs through prior dissociation to produce thallium triacetate.

Oxidations of a variety of substrates by lead tetraacetate[3] and mercuric acetate[4–6] have been studied extensively. By comparison, thallium triacetate which was first reported by Meyer[7] in 1903 has been used only in recent years and on a relatively limited scale. The reduction potential of the thallium(III) is between those of mercury(II) and lead(IV),[8] and thallium appears immediately between mercury and lead in the periodic table. It is surprising that oxidations by thallium(III) salts have not been investigated more extensively as they would be expected to be more selective than lead(IV) salts. Thallium triacetate or other carboxylate salts have been used for the oxidation of phenols,[9] thallation of aromatic compounds,[10] and reactions with olefins[11–17] and organomercury compounds.[18,19] Kabbe[11] reported in a limited comparative study that the properties of thallium triacetate are between those of lead tetraacetate and mercuric acetate.

In oxymercuration of olefins, the mercuric acetate addition product can easily be isolated[4] but only two adducts have been isolated and characterized with thallium triacetate.[11,15] The corresponding lead tetraacetate adduct with double bonds has yet to be isolated and characterized, although an adduct has been postulated to explain kinetic data for the reaction with anethole.[20] Winstein[15] isolated a very unstable solid, presumably the adduct, from the reaction of lead tetraacetate with norbornadiene, but was not able to characterize it.

The products from the reactions of olefins with those acetates of Hg(II), Tl(III), and Pb(IV) are pictured as proceeding through an addition adduct which is either isolatable or decomposes, *via* a carbonium ion, to yield organic products and lower valent metal species. The observed order of stability of the adducts is consistent with the respective oxidation potentials of the metal acetates. While there is semiquantitative information about the second step in the oxidation of olefins, there exists no complete comparison of the first step which is related to the relative electrophilicities of the metal acetates. Quantitative studies of the electrophilicity of the acetates of Hg(II), Tl(III), and Pb(IV) in a common system would provide a much needed comparison of the salts, and our efforts are directed toward that goal. Cyclopropanes have been chosen as electrophilic centers for these studies, and the previous paper in this series dealt with their oxidative cleavage by $Hg(OAc)_2$.[1] We now report our observations of the cleavage of phenylcyclopropanes by $Tl(OAc)_3$.



$$\mathrm{>C{=}C<} + \mathrm{M(OAc)}_x \longrightarrow \mathrm{-}\underset{\mathrm{AcO}}{\overset{|}{\underset{|}{\mathrm{C}}}}\mathrm{-}\underset{\mathrm{M(OAc)}_{x-1}}{\overset{|}{\underset{|}{\mathrm{C}}}}\mathrm{-} \longrightarrow \text{products} + \mathrm{M(OAc)}_{x-2}$$

Results

Thallium Triacetate. Our attempts to obtain pure thallium triacetate by Meyer's method initially were

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

[2] This research was supported by Grants GP3873 and GP6778 from the National Science Foundation. A portion of this paper was taken from the Ph.D. Thesis of A. South, Jr., The Ohio State University, 1966.

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

[4] J. Chatt, *Chem. Rev.*, 48, 7 (1951).

[5] R. E. Dessy and W. Kitching, *Advan. Organometal. Chem.*, 4, 289 (1966).

[6] K. Ichikawa, *Kogyo Kagaku Zasshi*, 66, 1037 (1963).

[7] R. J. Meyer and E. Goldschmidt, *Ber.*, 36, 238 (1903).

[8] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

[9] E. Hecker and R. Lattrell, *Ann.*, 662, 48 (1963).

[10] V. P. Glushkova and K. A. Kocheshkov, *Bull. Akad. Nauk SSSR*, 1211 (1957).

[11] H. J. Kabbe, *Ann.*, 656, 204 (1962).

[12] R. R. Grinstead, *J. Org. Chem.*, 26, 238 (1961).

[13] C. B. Anderson and S. Winstein, *ibid.*, 28, 605 (1963).

[14] P. M. Henry, *J. Am. Chem. Soc.*, 88, 1597 (1966); 87, 990, 4423 (1965).

[15] K. C. Pande and S. Winstein, *Tetrahedron Letters*, 3393 (1964).

[16] J. B. Lee and M. J. Price, *Tetrahedron*, 20, 1017 (1964).

[17] J. B. Lee and M. J. Price, *Tetrahedron Letters*, 3393 (1964).

[18] V. P. Glushkova and K. A. Kocheshko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1193 (1957).

[19] V. P. Glushkova and K. A. Kocheshko, *Bull. Akad. Nauk SSSR*, 1217 (1957).

[20] K. Ichikawa, Y. Takeuchi, and O. Itho, *Bull. Inst. Chem. Res.*, 40, 317 (1962).

unsuccessful. At 118°, the dissolution of thallic oxide in acetic acid containing acetic anhydride is rapid but the total thallium(III) content of the reaction is 36%. By successively lowering the temperature of the reaction it was possible to obtain a 90% thallium(III) titer at 50°. Instead of adding acetic anhydride to remove the water formed in the reaction of thallic oxide with acetic acid, water was added. As the water content increases, the reaction time decreases, and the thallium(III) content of the crude product remains at approximately 95%.

The kinetics of decomposition of thallium triacetate in anhydrous acetic acid were studied at 75.3 and 99.3° using an iodide–thiosulfate method described in the Experimental Section. These studies were necessary in order to ascertain whether the rate of cleavage of cyclopropanes could be studied conveniently without a complicated simultaneous destruction of the thallium triacetate. The simplest expression, with which the data from the decomposition of thallic acetate can be interpreted, is that of a one-fourth-order rate law. A much more complex expression is not ruled out, but present data do not allow a rigorous treatment. This limited kinetic study shows that the rate of decomposition of thallium triacetate is sufficiently slow, so as not to interfere with the kinetics of cleavage of phenylcyclopropanes by thallium triacetate.

Product Analysis. Substituted phenylcyclopropanes were cleaved with thallium triacetate in anhydrous acetic acid at 75° using 50% excess cyclopropane. The products were analyzed using gas chromatography and nuclear magnetic resonance. The only two products observed in each reaction were cinnamyl acetates and 1-aryl-1,3-propanediol diacetates. The per cent composition for the products of each reaction is listed in Table I. Analysis by nmr consisted of expanding the allylmethylene doublet of the cinnamyl acetates, *ca.* τ 5.4, and the benzal hydrogen triplet of the diacetates, *ca.* τ 4.2. Areas of the peaks from several spectra of each reaction mixture were averaged and corrected to area per hydrogen. Because of inherent experimental limitations, the vpc analysis is considered more reliable. However, the nmr analysis served as a check against the possibility that the products were cracking or polymerizing under chromatographic conditions. The results show that no significant decomposition occurs.

Table I. Substituted Phenylcyclopropane Cleavage Products from Thallium Triacetate

Substituent	Yield of cinnamyl acetate, % Vpc	Yield of cinnamyl acetate, % Nmr	Yield of 1-aryl-1,3-diacetoxypropane, % Vpc	Yield of 1-aryl-1,3-diacetoxypropane, % Nmr
p-MeO	7	5	93	95
p-Me	7.5	6	92.5	94
m-Me	9	7	91	93
H	10	9	90	91
p-Cl	8	7	92	93
m-Cl	5	4	95	96

Kinetic Analysis. The kinetics of the reaction of thallium triacetate with substituted phenylcyclopropanes in anhydrous acetic acid were studied initially by following the disappearance of cyclopropane relative to an internal standard by gas chromatography. However, the method was found to be unsatisfactory as the kinetic aliquots had to be freed from the acetic acid in order to facilitate analysis. In general the results were inaccurate because of the volatility of the cyclopropanes. In spite of the scatter, second-order kinetic plots for equimolar concentrations of the two reactants clearly exhibit dramatic curvature (Figure 1).

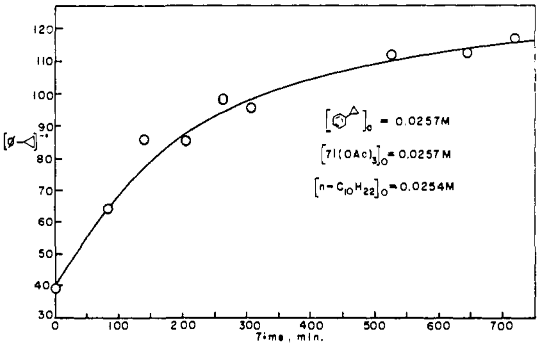

Figure 1. Curve for second-order plot at 50.1° for phenylcyclopropane concentration by vpc analysis.

The reduction of thallium(III) with excess standard ferrous solution followed by back titration of the excess ferrous ion with standard dichromate was examined, but the method was found not to be easily applicable for kinetic analysis. However, analysis of acetic acid solutions of thallium triacetate was accomplished by the addition of excess aqueous potassium iodide which results in the formation of thallium triiodide.[21] The triiodide is then titrated with standard sodium thiosulfate solution using a starch indicator. The rate of disappearance of thallium(III) by iodimetry was shown to be the same as the rate of loss of phenylcyclopropane as monitored by vpc for 0.015 *M* solutions at 50.1°. Second-order plots for equimolar concentrations of reagents showed an initial rapid loss of oxidative titer of the solution followed by a drastic slowing of the rate. The curve was of the same type as noted for the disappearance of cyclopropane. *The rate of disappearance of cyclopropane corresponds to the change in oxidative titer of the solution.* A double salt, $Tl_2(OAc)_4$, is produced in the reaction. The analytical method employed yields only the total concentration of thallium(III) species. Thus the change in the oxidative titer of the solution is not equivalent to the change in the concentration of free thallium triacetate.

$$TlOAc + Tl(OAc)_3 \rightleftharpoons Tl^{+}Tl(OAc)_4^{-}$$

In order to derive a rate expression, it was assumed that the equilibrium constant is very large in the direction of the double salt and that only thallium triacetate reacts with the cyclopropane in the rate-determining step. In addition, it was assumed that thallous acetate is produced rapidly after cleavage of the cyclopropyl ring, such that for every mole of thallium triacetate which is reduced another becomes inactive by double salt formation. The change in oxidizing power of the solution is equal to the amount of cyclopropane cleaved products which is designated as x. The cyclopropane remaining is $B_0 - x$, where B_0 is the initial concentration of cyclopropane. The total thallium(III) species as indicated by titration must

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[21] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p 337.

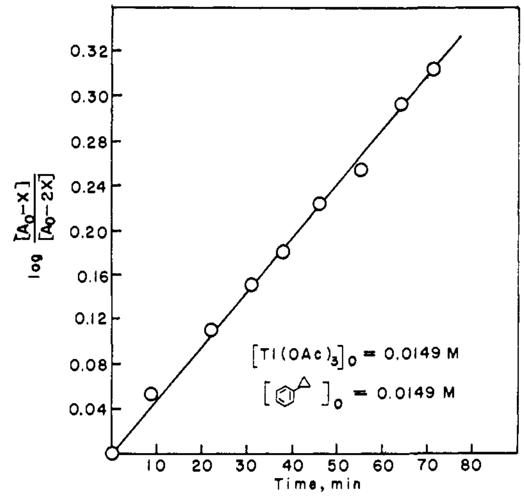


Figure 2. Second-order plot for equimolar initial concentrations of phenylcyclopropane and thallium triacetate at 50.1° with double salt formation.

be mathematically separated into free thallium triacetate and thallous–thallic acetate double salt. The free thallium triacetate is equal to $A_0 - 2x$, where A_0 is the initial concentration of thallium triacetate. The following rate law and integrated expressions were derived for the case $A_0 = B_0$. Plots using these expressions are straight lines (Figure 2). The expression is valid up to 50% reaction on the basis of phenylcyclopropane.

$$dx/dt = k(A_0 - 2x)(B_0 - x)$$

$$\log \frac{A_0 - x}{A_0 - 2x} = \frac{A_0 k}{2.303} t$$

A twofold excess of thallium triacetate allows the reaction to be followed to a greater per cent completion with respect to the phenylcyclopropane. The rate law and integrated expressions for the case $A_0 = B_0$ are

$$dx/dt = k(A_0 - 2x)(A_0/2 - x)$$

$$1/(A_0 - 2x) = kt + (1/A_0)$$

When a twofold excess of thallium triacetate was used, straight line plots were obtained over two half-lives for the function $1/(A_0 - 2x)$ *vs.* time (Figure 3). The observed rate constants from this treatment are slightly concentration dependent with the rate constant increasing as the initial concentration of thallium triacetate decreases (Table II).

Table II. Rate Constants for the Cleavage of Arylcyclopropanes with Thallium Triacetate

X	Arylcyclopropane, mol/l.	$Tl(OAc)_3$, mol/l.	Temp, °C	k, l./(mol min)
p-CH_3O	0.01561	0.01561	50.1	204[a]
p-CH_3	0.01492	0.02986	50.1	14.6
m-CH_3	0.01583	0.03170	50.1	1.64
H	0.01606	0.03222	29.6	0.172[b]
	0.01508	0.03021	50.1	0.65[b]
	0.00530	0.01063	50.1	0.81
	0.01576	0.03155	76.2	3.03[b]
p-Cl	0.01492	0.02988	50.1	0.188
m-Cl	0.01540	0.03055	50.1	0.0110

[a] This rate constant was determined from $k/K = 0.236$ in the presence of 0.04682 M added initial thallous acetate. This procedure had to be employed since the rate of the reaction is too rapid to be followed using the same experimental conditions as for the other arylcyclopropanes. [b] These rates were used to calculate $\Delta H^{\neq} = 12.4 \pm 0.2$ kcal/mol and $\Delta S = -29.2 \pm 0.6$ eu.

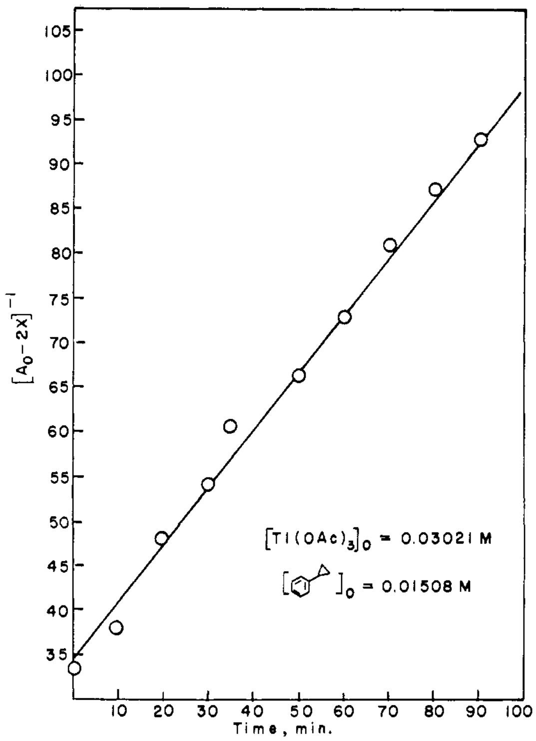


Figure 3. Typical plot at 50.1° for a 2:1 molar ratio of thallium triacetate to phenylcyclopropane.

Equilibrium Constant for Double Salt Formation. The equilibrium constant of the double salt formation was determined by kinetic studies of the cleavage of cyclopropanes by thallous–thallic acetate mixtures. Using the previously outlined assumptions, the following expression is derived, where S_0 and I_0 are the initial concentrations of thallous–thallic acetate double salt and excess thallous acetate, respectively, and B_0 is again the initial concentration of phenylcyclopropane.

$$\text{rate} = k[Tl(OAc)_3][\text{phenylcyclopropane}]$$

$$K = \frac{[Tl^+Tl(OAc)_4^-]}{[Tl(OAc)_3][TlOAc]}$$

$$\frac{dx}{dt} = \frac{k}{K}\frac{[Tl^+Tl(OAc)_4^-][\text{phenylcyclopropane}]}{[TlOAc]}$$

$$\frac{dx}{dt} = \frac{k}{K}\frac{(S_0 - x)(B_0 - x)}{I_0 + 2x}$$

The concentration of thallium species in the +3 oxidation state is approximately $S_0 - x$ when excess TlOAc is present. When the initial concentrations of phenylcyclopropane and the double salt are equal, the integrated rate expression is

$$\frac{I_0 + 2S_0}{2.303}\frac{1}{S_0 - x} + 2\log(S_0 - x) = \frac{1}{2.303}\frac{k}{K}t + \text{constant}$$

Increasing the ratio of thallous acetate to thallium triacetate initially added decreases the rate of loss

Table III. Time for 25% Reaction as a Function of Initial Thallous to Thallic Acetate Ratio at 50.1°

TlOAc/Tl(OAc)$_3$	t (25% reaction), min
0	50
1.00	225
1.29	420
1.50	460
2.00	585
3.00	1055
10.01	3600

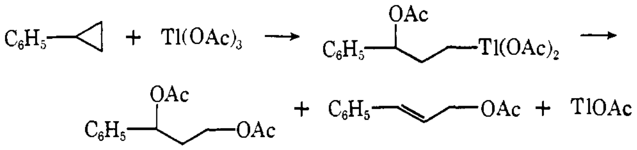
Table IV. Observed k/K Ratios for the Reaction of Phenylcyclopropane with Initial Thallous–Thallic Acetate Ratios

T, °C	Phenylcyclopropane, mol/l.	Tl(OAc)$_3$, mol/l.	TlOAc, mol/l.	TlOAc/ Tl(OAc)$_3$	$(k/K) \times 10^4$, min^{-1}	K, l./mol
50.1	0.01501	0.01520	0.03010	2.00	7.4	
50.1	0.01821	0.01823	0.05463	3.00	7.5	870
50.1	0.02284	0.02284	0.2287	10.01	7.7	
76.2	0.0195	0.0197	0.09784	4.96	80	380

of the thallium(III). This trend is shown in Table III in terms of times necessary for 25% reaction as a function of the initial ratio of added thallous acetate to thallium triacetate. Plots of the above expression *vs.* time gave straight lines (Figure 4) and k/K values were calculated. The data extending over a fivefold range of concentration ratios are listed in Table IV. The equilibrium constants are also listed in the table.

Discussion

The cleavage of arylcyclopropanes by mercuric acetate occurs to yield an adduct which is stable under the reaction conditions. The organomercury compounds do decompose at higher temperatures to produce cinnamyl acetates. Accordingly the reaction of thallium triacetate is postulated to occur *via* an organothallium intermediate which is unstable under the reaction conditions. The decomposition step involves a reduction of the metal site. The solvolytic instability of the organothallium intermediate as compared to the mercury analog is consistent with the relative reduction potential for Hg^{2+} and Tl^{3+}. In addition these results are in accord with the corresponding reactions of mercuric acetate and thallium triacetate with olefins in which the mercury adducts are much more stable than the thallium adducts. There are striking similarities between the organic products of olefin oxidation and cyclopropane oxidation.[22] The per cent yields of 3-acetoxycyclohexene obtained from oxidation of cyclohexene by mercuric acetate[23] and thallium triacetate are 100 and 11%, respectively. The decomposition of 3-phenyl-3-acetoxypropylmercuric acetate produces only cinnamyl acetate whereas the oxidative cleavage of phenylcyclopropane by thallium triacetate produces a 10% yield of cinnamyl acetate. There are consistent differences between the nature of carbon–metal bonds in the organometallic derivatives and the intermediate carbonium ion derived from solvolysis of these bonds.



We initially reported in an earlier communication[24] that there was evidence that the organothallium derivatives are detectable under the reaction conditions. However, the small concentration of reported product alcohol which was presumed to be formed in the aqueous work-up is actually the result of the reaction of the carbonium ion with water present in the acetic acid. The alcohol is gradually transformed to the acetate by acetic acid. The water in the acetic acid resulted from the formation of thallium triacetate from thallic oxide in the reaction medium. Therefore our statement that both steps of the oxidative cleavage reaction "proceed at measurable rates" must be modified. There is no proof from product analysis studies that the intermediate accumulates significantly under the present reaction conditions. The second step is faster than the cleavage step as required by our kinetic analysis in which thallous acetate must be formed shortly after the rate-determining cleavage step.

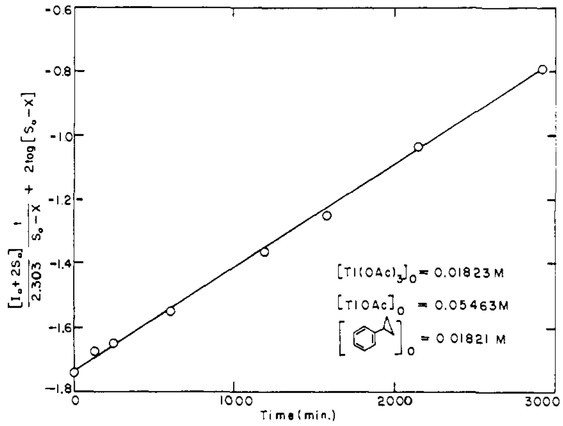


Figure 4. Typical plot for evaluation of k/K at 50.1°.

The instability of the organothallium derivative obtained from the addition of thallium triacetate to a cyclopropane ring is consistent with the observations made by Henry[14] on olefin adducts. The formation of glycols and carbonyl products from the oxythallated adduct occurs after the rate-determining addition step.

Electrophilic Agent. The oxidation of olefins by thallium triacetate in aqueous acetic acid has been studied extensively by Henry.[14] By pH measurements the equilibrium constants for both ionization of one acetate ion and coordination of one acetate ion have

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[22] R. J. Ouellette and R. D. Robins, *Tetrahedron Letters*, 397 (1968).

[23] N. N. Vorgaftik and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 5, 930 (1962).

[24] R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Am. Chem. Soc.*, 87, 2602 (1965).

been calculated. The only important reactive species over a wide concentration range is $Tl(OAc)_2^+$. Both $Tl(OAc)_3$ and $Tl(OAc)_4^-$ are found to be unreactive with respect to the cationic specie.

An extrapolation of Henry's data to our system is not possible in a quantitative manner. The solvent system used in the olefin oxidation was approximately 1 *M* acetic acid in water. In pure acetic acid the concentration of free ions must be very low and the reactive species that must be considered are $Tl(OAc)_3$ and the ion paired $Tl(OAc)_2^+OAc^-$. By analogy with Henry's observations it would be anticipated that the ion paired material should react more rapidly with a cyclopropane ring than would the covalent material. However, the relative quantities of the two potential electrophiles must be considered.

Kresge[25] has estimated the equilibrium constant for ion pair formation from mercuric acetate in acetic acid. The value of 2×10^{-8} for $K_i^{HgOAc^+OAc^-}$ is only

$$Hg(OAc)_2 \underset{}{\overset{K_i^{HgOAc^+OAc^-}}{\rightleftharpoons}} HgOAc^+OAc^-$$

approximate and is calculated from several approximate quantities. However, from studies of aromatic mercuration by $Hg(OAc)_2$ and $HgOAc^+ \; ClO_4^-$ it has been concluded that $Hg(OAc)_2$ is 10^{-4} less reactive than $HgOAc^+OAc^-$. Thus in the aromatic mercuration reaction the electrophilic agent is $Hg(OAc)_2$ in spite of its lower reactivity with respect to $HgOAc^+OAc^-$. The magnitude of the uncertainty in the value of K_i is not significant enough to allow any substantial fraction of the reaction to proceed from $HgOAc^+OAc^-$ as the electrophilic agent.

A qualitative comparison of $Tl(OAc)_3$ and $Hg(OAc)_2$ is possible. The formation constants of Tl(III) are larger than for Hg(II) although the number of examples are limited.[26] However, a similar ordering occurs for Cd(II) and In(III). In addition the order of formation constants is consistent with changes in ion charge and radius. Therefore, the formation of ion pairs should be less favorable for $Tl(OAc)_3$ than for $Hg(OAc)_2$. The

$$Tl(OAc)_3 \overset{K_i^{Tl(OAc)_2^+OAc^-}}{\rightleftharpoons} Tl(OAc)_2^+OAc^-$$

ion pair formation constants for $Hg(OAc)_2$ and $Tl(OAc)_3$ involve changes of the same charge type. Only the ion size of the central metal atom should contribute to any net difference.

Since it appears unlikely that any significant amount of $Tl(OAc)_2^+OAc^-$ exists in acetic acid, it can be concluded that the cleavage of cyclopropanes proceeds *via* the covalent $Tl(OAc)_3$. This conclusion is based on a reasonable analogy with Kresge's observations on the relative reactivities of $Hg(OAc)_2$ and $HgOAc^+OAc^-$. The relative reactivities of $Tl(OAc)_3$ and $Tl(OAc)_2^+OAc^-$ should stand in the ratio of $1:10^4$. The change in the electrophilicity of the covalent and ion paired material for the two metal acetates are directly comparable in terms of ligand types and charge alteration. There should be a minor statistical change in the electrophilicity ratio as a result of orbital availability. If there are any unrecognized contributions to the reactivity ratios, the change for $Tl(OAc)_3$ would have to be at least three powers of ten greater than measured for $Hg(OAc)_2$ in order to allow any significant attack of cyclopropane by $Tl(OAc)_2^+OAc^-$. In our opinion, such a change is unreasonable.

Henry[14] estimated that the reactivity of $Tl(OAc)_3$ in water cannot be greater than 0.05 that of $Tl(OAc)_2^+$. If this value were exceeded there would not have existed as good an agreement between calculated and experimental rate constants. His approximation provides another limit for our estimation of the reactivity of $Tl(OAc)_2^+OAc^-$ with respect to $Tl(OAc)_3$. The reactivity of $Tl(OAc)_2^+$ in water undoubtedly is lowered as the result of solvation by water. Therefore, if the reactivity ratio of $Tl(OAc)_2^+$ to $Tl(OAc)_3$ could have been determined in water, the reactivity ratio of $Tl(OAc)_2^+OAc^-$ to $Tl(OAc)_3$ in acetic acid should be larger than that value. Credence is lent to this argument by the observation that $Tl(OAc)_2^+$ is similar in reactivity to Tl^{3+} in water as solvent. Henry indicates that the similarity in rates in spite of charge differences attests to the solvation of the ions by water. In addition, a strong acceleration of rate of oxidation of ethylene is obtained by lowering the water activity. Therefore, we feel that Kresge's reactivity ratio for $Hg(OAc)_2$ in acetic acid is consistent with all of the available data for $Tl(OAc)_3$ in aqueous acetic acid and our reaction must proceed *via* covalent $Tl(OAc)_3$.

Comparative Reactivity of Metal Acetates. The second-order rate constants for cleavage of phenylcyclopropane by thallium triacetate and mercuric acetate at 25° are 2.0×10^{-3} and 1.7×10^{-4} l./mol sec, respectively. Therefore, mercuric acetate and thallium triacetate are of similar electrophilic reactivity. Mercuric acetate and thallium triacetate both can act as Lewis acids, for they are coordinatively unsaturated if acetate is considered as a monodentate ligand. In acetic acid both compounds may be four coordinate with the solvent occupying the remaining coordination sites. When these two salts serve as electrophiles, it is likely that acetic acid would be replaced in preference to an acetate ion. Therefore, the similarity of the two salts remains, and it is still convenient to consider them coordinatively unsaturated and able to act as effective electrophiles with respect to the cyclopropane ring bond as a base. The order of reactivities of mercuric acetate and thallium triacetate probably is related to the higher oxidation state or nuclear charge of the latter compound.

Effect of Substrate Structure. The effect of substrate structure on the cleavage reaction is distinct as illustrated by $\rho = -4.3$ (Figure 5). In the electrophilic attack on the cyclopropane ring a positive charge is generated at the benzyl position.[27] By comparison, the

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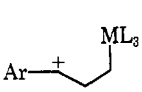
(25) A. J. Kresge, M. Dubeck, and H. C. Brown, *J. Org. Chem.*, 32, 745 (1967).

(26) L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964.

(27) The *p*-methoxyphenylcyclopropane datum point is significantly slower than it should be according to the correlation line drawn through the other data points. The reaction has a half-life of a few minutes under the conditions used to determine the rate constant. A partitioned flask was used to determine a series of one-point kinetic determinations. However, we feel the analytical method is valid and cannot account for the observed deviation from the correlation line. A possible explanation of the deviation involves the relative rates of the cleavage step and the solvolytic step. In the case of the other arylcyclopropanes the cleavage step is rate determining and the solvolytic step is rapid resulting in the decrease in the oxidative titer of the system. For the *p*-methoxy compound the two rates may become comparable and the observed change in the oxidative titer of the solutions would be slower than the actual rate of cleavage if the intermediate is titratable.

$\rho = -3.2$ for mercuric acetate indicates a smaller positive charge at the benzyl position. The ρ for each metal acetate indicates the discriminatory power of the electrophile. In electrophilic aromatic substitution, it has been observed that for a series of related electrophiles the discriminatory power is inversely related to reactivity of the species. This trend can be rationalized by use of the Hammond postulate. For our system of electrophilic attack on a cyclopropane ring a positive charge is generated at a benzyl position, and the response in the rate as a function of substituent should be a function of the reactivity of the attacking reagent. The discrimination of thallium triacetate is higher than for mercuric acetate although the former reacts at a faster rate. Thus the more rapid apparent reaction is associated with the most discriminatory process. A possible explanation for this reversal of the selectivity–reactivity relationship may involve the ligands coordinated to the metal in the following generalized transition state, where M represents the metal and L may be any ligand. For mercuration of cyclopropane two of the ligands are acetate and one is acetic acid,



whereas in thallation all of the ligands are acetate. Mercury may then provide a local solvent molecule to provide partial stabilization of positive charge in the transition state. In addition, considering the ligand acetate in both mercury and thallium, that of mercury should be more readily available for local stabilization of positive charge. This order of availability of ligands is consistent with trends in formation constants.

Activation Parameters. The activation parameters for the cleavage reaction of phenylcyclopropane by thallium triacetate ($\Delta H^{\ddagger} = 12.4$ kcal/mol, $\Delta S^{\ddagger} = -29.2$ eu) are distinctly different from those for mercuric acetate ($\Delta H^{\ddagger} = 19.1$ kcal/mol, $\Delta S^{\ddagger} = -11.7$ eu). In spite of the postulate that both of the reactions proceed *via* covalent metal acetates, the remarkably different activation parameters can be accepted comfortably if solvation differences are considered. The degree of solvation of the metal acetates in solution, the substitution process of a cyclopropane ligand replacing solvent or acetate ion in the coordination sphere, and stabilization of positive charge in the transition state by local solvent ligands can all contribute to the observed differences in activation parameters. The definition of the magnitude of each of the contributing terms is beyond the scope of this study.

Double Salt Formation. The equilibrium constants for double salt formation at 50 and 76.2° are 870 and 380 l./mol, respectively. At 25° the extrapolated formation constant is 2000 l./mol. In aqueous acetic acid at 25° the formation constant is 209 l./mol.[14] The difference in these two numbers must reflect the great difference in the solvent polarities. The magnitude of our values in acetic acid indicates that the kinetic analysis using added thallous acetate is mathematically correct within experimental error. The values of S_0 and I_0 used in obtaining k/K data are approximately 1% too high for TlOAc = 0.2287 M and 3% too high for TlOAc = 0.03010 M. Thus the small drift in apparent k/K values is the result of approximations made in calculating initial concentration for free thallous acetate and the double salt. There is, therefore, no kinetic evidence that the double salt is capable of acting as an effective electrophile in the presence of even small concentrations of thallium triacetate. The species is coordinatively saturated and its lack of reactivity must reflect a reluctance to allow displacement of acetate by a cyclopropane ligand. Assuming that a 5% rate contribution due to the double salt could be detected, the reactivity of double salt must be less than 10^{-3} that of $Tl(OAc)_3$.

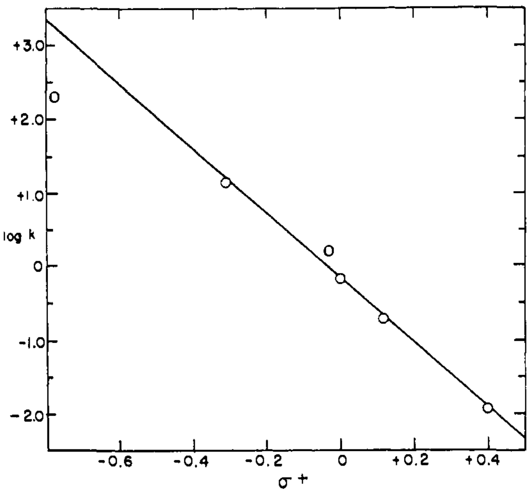


Figure 5. Hammett σ^+ correlation at 50.1°.

The drift in the rate constant for runs in which only thallium triacetate was initially present can now be explained. The extent of dissociation of the double salt is experimentally significant. Therefore the calculated rate constants are not true rate constants, as they are dependent on a mathematical partitioning of the oxidation titer of the system into free thallium triacetate and the double salt. Only under conditions of high initial thallium triacetate concentration are the rate constants meaningful. The data for the 0.03 M concentrations used in this study are within 15% of the true rate constants that could be derived by instantaneous rate studies employing calculated $Tl(OAc)_3$, TlOAc, and $Tl_2(OAc)_4$ concentrations.

Experimental Section

Preparation of α-Arylallyl Acetates. The α-arylallyl alcohols described in the previous paper[1] were acetylated by acetyl chloride in an ethereal solution containing pyridine similar to the method of Braude.[28] All of the esters exhibit complex absorptions at τ 3.7–4.3 (1 H) and 4.6–5.0 (3 H) in addition to the aromatic and acetate methyl protons. The elemental analysis of the previously unknown compounds are given in Table V.

Table V. Elemental Analyses of α-(Substituted phenyl)allyl Acetates

	Calcd, %			Found, %		
X	C	H	Cl	C	H	Cl
p-MeO	69.88	6.84		69.62	6.80	
p-Me	75.76	7.42		75.71	7.30	
m-Me	75.76	7.42		75.86	7.43	
p-Cl	62.72	5.26	16.84	62.49	5.27	16.78
m-Cl	62.72	5.26	16.84	62.51	5.26	16.75

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(28) E. A. Braude, D. W. Turner, and E. S. Waight, *J. Chem. Soc.*, 2396 (1958).

Rearrangement of α-Phenylallyl Acetate. A solution of 0.1 g (0.00057 mol) of α-phenylallyl acetate in 5 ml of anhydrous acetic acid in a sealed tube was allowed to stand at 75° for 120 hr. The reaction mixture was dissolved in ether and washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Analysis of the remaining liquid by nmr in carbon tetrachloride showed a doublet at τ 5.4 (2 H), multiplet at 3.2–4.1 (2 H), singlet at 2.7 (5 H), and acetate methyl at 8.0 (3 H). This spectrum is identical with cinnamyl acetate. The complex pattern at τ 4.6–5.05 (3 H) in the starting α-phenylallyl acetate was absent.

Rearrangement of α-Arylallyl Acetates. The *m*- and *p*-chloro-, *m*- and *p*-methyl-, and *p*-methoxyphenylallyl acetates also rearranged to the corresponding cinnamyl acetates under the conditions described above. The rearrangements were quantitative except for *m*-chlorphenylallyl acetate on the basis of nmr analysis. All of the reaction mixtures showed a doublet at τ 5.4, multiplet at 3.2–4.1, and acetate methyl at 8.0. The *m*-chloro compound also showed the complex absorptions at τ 4.6–5.05 from the *m*-chlorophenylallyl acetate.

Preparation of Cinnamyl Acetate. To a solution of 13.4 g (0.01 mol) of cinnamyl alcohol and 15 ml (14.7 g, 0.19 mol) of pyridine in 125 ml of anhydrous ether was added dropwise with stirring a solution of 10 ml (11 g, 0.16 mol) of acetyl chloride in 10 ml of anhydrous ether. The mixture was stirred at room temperature for 24 hr after which time water was added and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was distilled through a 15-cm Vigreux column. A yield of 82% of 14.5 g (0.082 mol) of cinnamyl acetate was obtained, bp 133° (11 mm) (lit.[29] bp 115° (2.5 mm)). Analysis by nmr in carbon tetrachloride showed a doublet at τ 5.4 (2 H), multiplet at 3.2–4.1 (2 H), singlet 2.7 (5 H), and singlet 8.0 (3 H).

Preparation of Substituted Cinnamyl Acetates. The identical procedure as described for the preparation of cinnamyl acetate was used for the substituted compounds. The *m*- and *p*-methyl compounds are known.[30,31] The structures of the methoxy and chloro-compounds were confirmed by the characteristic nmr spectra.

Preparation of Ethyl 3-Hydroxy-3-(*p*-tolyl)propionate. To 8 g (0.12 mol) of powdered zinc was added dropwise with stirring a solution of 12 g (0.1 mol) of *p*-tolualdehyde and 12 ml (18.2 g, 0.11 mol) of ethyl bromoacetate in 16 ml of dry benzene and 4 ml of anhydrous ether. The mixture was stirred under reflux in a nitrogen atmosphere for 6 hr and then cooled in an ice bath. To the mixture was added 40 ml of cold 10% sulfuric acid with vigorous stirring. The layers were separated, and the organic layer was washed twice with 3-ml portions of cold 5% sulfuric acid, once with saturated sodium bicarbonate solution, and finally with water. The washings were combined and extracted twice with ether. The ether extracts were combined with the organic layer, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm Vigreux column. A yield of 69% of 14.3 g (0.069 mol) of ethyl 3-hydroxy-3-(*p*-tolyl)propionate was obtained, bp 111–112° (0.35 mm). Analysis by nmr showed a triplet (1 H) at τ 5.1, a doublet (2 H) at 7.5 and the ethyl triplet and quartet at 8.85 and 6.0, respectively.

Preparation of Ethyl 3-Hydroxy-3-arylpropionates. The ethyl 3-hydroxy-3-(substituted phenyl)propionates were prepared as in the above described procedure. The same nmr absorptions as listed in the preceding procedure are present in spectra of the other substituted compounds. The *p*-methoxy compound was not distilled in order to avoid dehydration. The *m*-methyl compound was prepared in 52% yield, bp 103–105° (0.2 mm), and the *p*-chloro compound in 42% yield, bp 134–136° (0.3–4 mm). None of the ethyl 3-hydroxy-3-arylpropionates were purified sufficiently for analytical samples.

Preparation of 1-(*p*-Tolyl)-1,3-propanediol Diacetate. To a slurry of 2 g (0.052 mol) of lithium aluminum hydride in 100 ml of anhydrous ether was added dropwise a solution of 10.4 g (0.05 mol) of ethyl 3-hydroxy-3-(*p*-tolyl)propionate in 10 ml of anhydrous ether. The mixture was stirred under reflux for 24 hr, hydrolyzed with water, and suction filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated.

A solution of the 1-(*p*-tolyl)-1,3-propanediol and 13 ml (12.8 g, 0.16 mol) of pyridine in 125 ml of anhydrous ether was acetylated with 12 ml (11.9 g, 0.15 mol) of acetyl chloride. The mixture was stirred at room temperature for 36 hr, water was added, and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm Vigreux column. A yield of 74% of 9.32 g (0.037 mol) of 1-(*p*-tolyl)-1,3-propanediol diacetate was obtained, bp 124° (0.4 mm). Analysis by nmr showed a triplet at τ 4.3 (1 H), a multiplet at 6.0 (2 H), and two acetate methyl groups at 8.03 and 8.07. Another multiplet appears under the acetate methyls.

Preparation of 1-Aryl-1,3-propanediol Diacetates. The 1-aryl-1,3-propanediol diacetates were prepared as described in the above procedure. All of the 1-phenyl-1,3-propanediol diacetates exhibit absorptions in their nmr spectra as listed in the preceding procedure. The *p*-methoxy diacetate was obtained in 29% yield (based upon *p*-anisaldehyde), bp 144–150° (0.25 mm). The *m*-methyl diacetate was collected from a vpc 5 ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb W column at 185°, 58% yield. *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.88; H, 6.84. The *p*-chloro diacetate was obtained in 70% yield, bp 136–138° (0.25 mm). *Anal.* Calcd for $C_{13}H_{15}O_4Cl$: C, 57.68; H, 5.58; Cl, 13.10. Found: C, 57.43; H, 5.53; Cl, 13.30.

Preparation of Ethyl Phenylacetate. A solution of 13.6 g (0.1 mol) of phenylacetic acid in 125 ml of absolute ethanol containing 1 ml of concentrated sulfuric acid was refluxed for 18.5 hr. The solution was poured over 300 ml of ice and water and the aqueous mixture was extracted with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining ester was vacuum distilled through a 15-cm Vigreux column. A 90% yield of 14.7 g (0.09 mol) of ethyl phenylacetate was obtained, bp 105–109° (14–15 mm) (lit.[32] bp 132–138° (32 mm)).

Preparation of Ethyl *p*-Anisyl- and *m*-Tolylacetates. Ethyl *p*-anisyl- and *m*-tolylacetates were prepared as described in the preceding method. Ethyl *p*-anisylacetate was obtained in 91% yield, bp 136–137° (11 mm) (lit.[33] bp 100–102° (1 mm)). Ethyl *m*-tolylacetate was prepared in 76% yield, bp 105–108° (11–12 mm) (lit.[34] 237–238°).

Preparation of Ethyl *p*-Tolylacetate. A solution of 35.2 g (0.25 mol) of *p*-tolylacetonitrile in 100 ml of 95% ethanol and 25 ml of concentrated sulfuric acid was refluxed for 7 hr. The mixture was allowed to cool and was poured over 300 g of ice and water. The aqueous mixture was extracted three times with ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm Vigreux column. A 68% yield of 30.2 g (0.17 mol) of ethyl *p*-tolylacetate was obtained, bp 111–3° (13–14 mm) (lit[35] bp 72–74° (0.9 mm)).

Preparation of Ethyl *p*- and *m*-Chlorophenylacetates. Ethyl *p*- and *m*-chlorophenylacetates were prepared as in the above procedure. A 75% yield of ethyl *p*-chlorophenylacetate was obtained, bp 107–108° (5 mm) (lit.[36] bp 260°). The *m*-chlorophenylacetate was not distilled.

Preparation of Diethyl Phenylmalonate. To 25 ml of absolute ethanol (distilled from sodium) was added 1.15 g (0.05 g-atom) of freshly cut sodium. After dissolution of the sodium, 7.31 g (0.05 mol) of diethyl oxalate was added in one portion immediately followed by the addition of 8.2 g (0.05 mol) of ethyl phenylacetate in one portion. The mixture was stirred until the solid enolate salt formed (10 min) and was suction filtered; the salt was washed with anhydrous ether. The salt was shaken with 2 ml of concentrated sulfuric acid in 25 ml of water and the mixture was extracted with ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was heated at 175° (15 mm) for 5 hr

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(29) M. Lora-Tamayo, F. Martin-Panizo, and R. Perez-Ossario, *J. Chem. Soc.*, 1418 (1950).

(30) H. Burton, *ibid.*, 1650 (1928).

(31) H. Burton and C. K. Ingold, *ibid.*, 904 (1928).

(32) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, 2nd ed, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, p 270.

(33) R. L. Huang and K. T. Lee, *J. Chem. Soc.*, 4299 (1955).

(34) M. Senkowski, *Monatsh. Chem.*, **9**, 855 (1888).

(35) A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, 80, 2844 (1958).

(36) R. Walter and A. Wetzlich, *J. Prakt. Chem.*, [2] 61, 196 (1900).

and then vacuum distilled through a 10-cm Vigreux column. A 37% yield of 4.36 g (0.19 mol) of diethyl phenylmalonate was obtained, bp 94–96° (0.07 mm) (lit.[37] bp 158–162° (10 mm)).

Preparation of Diethyl-Substituted Phenylmalonates. Diethyl-substituted phenylmalonates were prepared as described in the preceding method. The per cent yields and boiling points are listed in Table VI. The *m*-chlorophenylmalonate was not distilled because of the small quantity available.

Table VI. Per Cent Yields and Boiling Points of Diethyl-Substituted Phenylmalonates

X	Yield, %	Bp (mm), °C	Lit. bp (mm), °C
p-MeO	32	118–21 (0.05–0.08)	152–153 (2.5)[a]
p-Me	16	133–135 (1.25)	124–125 (1–2)[b]
m-Me	56	110–111 (0.25)	125–132° (2)[c]
p-Cl	52	124–126 (0.7–0.6)	178–180 (15)[d]

[a] J. B. Niedral, U. S. Patent 2,297,911 (Oct 6, 1943). [b] V. H. Wallingford and A. H. Homeyer, U. S. Patent 2,367,632 (Jan 16, 1945). [c] B. V. Zanten and W. T. Nauta, *Rec. Trav. Chim.*, **79**, 1211 (1960). [d] M. Carissimi, I. Grasso, E. Grumelli, E. Milla, and F. Ravenna, *Farmaco, Ed. Sc.*, **17**, 390 (1962).

Preparation of 2-Phenyl-1,3-propanediol Diacetate. To a slurry of 4.5 g (0.11 mol) of lithium aluminum hydride in 200 ml of anhydrous ether was added dropwise a solution of 23.6 g (0.1 mol) of diethyl phenylmalonate in 50 ml of anhydrous ether. The mixture was stirred under reflux for 25 hr, hydrolyzed with water, and suction filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

To a solution of the 2-phenyl-1,3-propanediol and 20 ml (19.6 g, 0.26 mol) of pyridine in 150 ml of anhydrous ether was added dropwise a solution of 18 ml (19.8 g, 0.25 mol) of acetyl chloride in 20 ml of anhydrous ether. The mixture was stirred at room temperature for 24 hr, water was added, and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The ester was vacuum distilled through a 15-cm Vigreux column. A 57% yield of 13.4 g (0.057 mol) of 2-phenyl-1,3-propanediol diacetate was obtained, bp 110–113° (0.3–0.35 mm) (lit.[38] bp 162–164° (13 mm)). Analysis by nmr showed a quintet at τ 6.75 (1 H), doublet at 5.75 (4 H), and acetate methyl groups at τ 8.05 (6 H).

Preparation of 2-(Substituted phenyl)-1,3-propanediol Diacetates. The 2-(substituted phenyl)-1,3-propanediol diacetates were prepared as described in the above procedure. Analysis by nmr showed the 2-phenyl-1,3-propyldiacetates to exhibit a quintet at τ 6.75 (1 H), doublet 5.75 (4 H), and acetate methyl at 8.05. The yields and boiling points are listed in Table VII and the elemental analyses are listed in Table VIII. The 2-(*m*-chlorophenyl)-1,3-propanediol diacetate was collected by vpc on a 5-ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb W column.

Table VII. Per Cent Yields and Boiling Points of 2-(Substituted phenyl)-1,3-propanediol Diacetates

X	Yield, %	Bp (mm), °C
p-MeO	50	152–153 (0.65)
p-Me	37	132 (0.75)
m-Me	38	156 (2.6)
p-Cl	53	118–121 (0.8)

Kinetics of Cleavage of Phenylcyclopropanes. The solutions for kinetic analysis were prepared by weighing an amount of the cyclopropane into a volumetrically measured amount of anhydrous acetic acid. From the weight of the cyclopropane, the desired amount of thallic acetate was calculated, weighed out, and added to the solution.

Table VIII. Elemental Analysis of 2-(Substituted phenyl)-1,3-propanediol Diacetates

	Calcd, %			Found, %		
X	C	H	Cl	C	H	Cl
p-MeO	63.15	6.81		62.90	6.71	
p-Me	67.18	7.25		66.84	7.40	
m-Me	67.18	7.25		66.98	7.20	
p-Cl	57.68	5.58	13.10	57.47	5.58	13.30
m-Cl	57.68	5.58	13.10	57.41	5.47	13.07

The methods of sampling were dependent upon the rate of cleavage. For extremely fast reactions partition flasks were used. Aliquots of each reactant were pipetted into opposite sides of the partition flask and allowed to equilibrate at the bath temperature, the solutions mixed by shaking so as to allow passage over the partition barrier. When the rate of cleavage was moderate and the temperature such that evaporation was not a complication, aliquots were pipetted from the reaction flask. For slow reactions and high temperatures, in which evaporation would be a complication, aliquots were sealed in test tubes.

The method of analysis consisted of quenching the aliquot in excess 5% aqueous potassium iodide. To the resulting yellow heterogeneous mixture was added a starch–iodine indicator. The dark mixture was titrated to a pure yellow mixture with standard sodium thiosulfate solution.

Monitoring the reaction by vpc with an internal standard was carried out by quenching aliquots in an ice–water mixture. The ice–water mixture was extracted with ether which was then washed several times with ice–water and finally with cold saturated sodium bicarbonate solution. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and carefully concentrated to a volume such that a 50-μl sample of the ether solution could be analyzed on a 10 ft × 0.25 in. 20% Apiezon J on 60–80 Chromosorb W vpc column. The decrease of the area of the cyclopropane peak was measured relative to the internal standard. The method of sampling was the same as described above. Preparation of the kinetic solutions was the same as described above except decane or dodecane, as internal standards, was weighed into the acetic acid solution of the cyclopropane.

Preparation of Thallium Triacetate as a Function of Temperature. The preparation of thallium triacetate obtained by the dissolution of *ca.* 0.05 g of thallic oxide in 10 ml of 0.18 *M* acetic anhydride in acetic acid was measured as a function of temperature. After complete reaction, the acetic acid was vacuum transferred and the remaining solid was dissolved in 25 ml of 1 *N* sulfuric acid. To the solution was pipetted 10 ml of 0.0889 *N* ferrous ammonium sulfate and the solution was allowed to stand under a nitrogen atmosphere for 2 hr. After addition of 10 drops of 86% phosphoric acid and 10 drops of 0.005 *M* diphenylamine sodium sulfonate, the solution was titrated with 0.100 *N* potassium dichromate to the purple end point. The results are listed in Table IX and each value is an average of two independent reactions which do not vary more than ±1.5%.

Table IX. Per Cent Thallium Triacetate as a Function of Temperature

Reaction time, hr	Temp, °C	$Tl(OAc)_3$ purity, %
60	50	90
23	60	80
6	75	68
0.75	100	60
0.17	118 (reflux)	36

Preparation of Thallium Triacetate as a Function of Per Cent Water. Time and per cent thallium triacetate obtained by the dissolution of *ca.* 0.05 g of thallic oxide in varying per cent aqueous acetic acid at 60° were determined. The same analytical procedure as described above was used and the results are listed in Table X. Each value is an average of two independent reactions which do not vary more than ±1.5%.

Preparation of Thallium Triacetate. A mixture of 10 g (0.022 mol) of thallic oxide in 100 ml of acetic acid and 25 ml of water was stirred at 50° for 4 hr. The residual solid was removed by suction

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(37) P. A. Levene and G. M. Meyer, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1943, p 288.

(38) H. J. Prins, *Chem. Z.*, **3**, 1001 (1919).

Table X. Per Cent Thallic Acetate as a Function of Per Cent Water at 60°

Reaction time, hr	H_2O added, %	Yield of $Tl(OAc)_3$, %
5.5	2	95
4	4	95
2	8	95
1.7	10	95

filtration. Most of the acetic acid was removed under reduced pressure. The solid was dissolved in a minimum amount of acetic acid at 75° and the thallic acetate crystallized upon cooling. The solid was suction filtered and dried under a continuous vacuum. A 73.7% yield of 12.3 g (0.032 mol) of thallic acetate was obtained and the dry solid stored in a desiccator. The thallium triacetate was found to be 98% pure by the previously described iodide–thiosulfate analytical procedure.

In another preparation a mixture of 15 g (0.033 mol) of thallic oxide in 100 ml of acetic acid and 15 ml of water was stirred for 21 hr at 55°. A yield of 65% of 99% pure thallic acetate was obtained.

Thallium triacetate exhibits no sharp decomposition or melting point to 200° but it does begin slow decomposition at *ca.* 75–80°.

Table XI. Apparent One-Third-Order Rate Constants for the Decomposition of Thallium Triacetate

$Tl(OAc)_3$, mol/l.	Temp, °C	$k \times 10^4$, $mol^{2/3}/l.^{2/3}$ min
0.0300	75.3	0.34
0.0305	99.3	3.9
0.0210	99.3	3.6
0.0156	99.4	3.6
0.0107	99.3	3.8

Preparation of Thallous–Thallic Acetate Double Salt. A solution of 0.527 g (0.0020 mol) of thallous acetate and 0.763 g (0.0020 mol) of thallic acetate in 15 ml of anhydrous acetic acid was concentrated under reduced pressure. The remaining white solid exhibits a sharp decomposition at 178–180° with no prior discoloration or melting.

Kinetics of Decomposition of Thallic Acetate. Solutions for kinetic analysis were prepared by dissolving the desired amount of thallic acetate in a volumetrically measured quantity of anhydrous acetic acid. Aliquots were sealed in test tubes and the iodide–thiosulfate procedure was used to analyze the aliquots. The rate constants for a one-third-order reaction are listed in Table XI.

Concerning the Mechanism of Hydrolysis of N-Methylacetimidate Esters[1]

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Contribution No. 1621 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received August 5, 1968*

Abstract: The rates of hydrolysis of 2,2,2-trifluoroethyl-, 2-methoxyethyl-, and ethyl N-methylacetimidate in aqueous solution have been investigated in the pH range 1–10 at 25°. At values of pH below 4, first-order rate constants for hydrolysis are independent of pH and increase markedly as the electron-withdrawing power of the alkoxy group increases: $\rho^* = 2.1$. Above pH 4, first-order rate constants for the ethyl and 2-methoxyethyl derivatives increase with increasing pH while those for the 2,2,2-trifluoroethyl substrate decrease with increasing pH. At values of pH above 8, the rate constants again are independent of pH and decrease slightly as the electron-withdrawing power of the alkoxy group increases: $\rho^* = -0.7$. Values of pK_a for the conjugate acids of the acetimidates determined titrimetrically and from the breaks in the pH–rate profiles are in good agreement: ethyl, 7.5; 2-methoxyethyl, 7.0; and 2,2,2-trifluoroethyl, 5.5. These results suggest that attack of water on the conjugate acids of the substrates is rate determining under acidic conditions and that attack of hydroxide ion on these species is rate determining under basic conditions. Under acidic conditions, each of the acetimidates decomposes to yield the corresponding esters quantitatively. As the pH is increased, the product distribution gradually changes until the corresponding amides are produced in near-quantitative yields above pH 10. The change in product distribution does not parallel the break in the pH–rate profile. The independence of the rate-determining and product-determining steps provides strong evidence for the existence of a tetrahedral intermediate in these reactions. Investigation of the effects of lithium chloride concentration on the kinetics of hydrolysis of phenyl N-methylacetimidate under acidic conditions reveals that the previously observed break in the pH–rate profile for this reaction near pH 2 is a consequence of a change in the activity of water and not of a transition in rate-determining step.

The elegant work of Schmir and his associates has provided strong evidence that hydrolysis of both cyclic and acyclic imidates proceeds through the formation of tetrahedral intermediates: (i) rate constants and product distributions are independent functions of pH,[4,5] and (ii) rate constants and product distributions are independent functions of buffer concentration.[4,6] Thus, the hydrolysis of imidates must be included in the group of nucleophilic reactions at acyl and carbonyl carbon for which reasonably strong evidence has been provided to support the concept of tetrahedral intermediates.[7,8]

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(2) National Defense Educational Act Predoctoral Fellow.

(3) Career Development Awardee of the National Institutes of Health (K3 GM 10-248-02). Fellow of the Alfred P. Sloan Research Foundation.

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