tight-fitting Teflon stopper and was then placed into the cell compartment of the ORD. The cell compartment was thermostated at 99.80 ± 0.5° through the use of an ethylene glycol filled circulating pump obtained from the Precision Scientific Co. The solution was allowed to equilibrate at this temperature for 30 min while the instrument was set at zero rotation at the sodium D line (5893 Å). The neat ester (5–15 mg) was introduced *via* a capillary tube and was stirred for 2 sec. The optical rotation of the solution was recorded continuously for a period of 6 hr (*ca.* 2 half-lives of reaction) and the rotation was found to decrease exponentially to a value of 0.00 after 20 hr. The products were acetophenone and 4-bromo-3,5-dimethylpyrazole in 99% yields by nmr and glc. A least-squares fit to the best straight line of ln (rotation) *vs.* time indicated that the decomposition of the ester was first order with a rate constant reproducible to ±3%.

Methyl 4-Nitrophenylcarbonate. Into the reaction vessel used for volumetric rate determinations was placed 0.540 g of methyl 4-nitrophenylcarbonate and 50 mg of tetra-*n*-butylammonium iodide. The reaction vessel was then placed into a flask containing vigorously boiling ethylene glycol (195°) and the gas buret was immediately attached to the reaction vessel. After 5 min 68 ml of carbon dioxide (identified by ir) was evolved, corresponding to 90% reaction. The reaction mixture was cooled to room temperature, and ether was added. The ether solution was washed with two 10-ml portions of water, dried over sodium sulfate, and concentrated *in vacuo*. The residue (0.375 g, 91% yield) was identified as 4-nitroanisole by comparison of the infrared and nmr spectra and melting point with those of authentic material.

Dimethyl Malonate Decarboxylation. Into a 50-ml round-bottom distilling flask was placed 25 g of dimethyl malonate and 1 g of tetra-*n*-butylammonium iodide. The mixture was heated with a heating mantle at atmospheric pressure with stirring. Near the boiling point of the malonate, evolution of carbon dioxide began and, after 30 min, methyl acetate began to distill from the reaction mixture. After 2.5 hr, 5 g of methyl acetate was collected (35% yield). The methyl acetate was identified by comparison of the ir and nmr spectra with those of authentic material.

Registry No.—Methyl chloroformate, 79-22-1; ethyl chloroformate, 541-41-3; isopropyl chloroformate, 108-23-6; benzyl chloroformate, 501-53-1; (*R*)-(+)-α-phenylethanol, 1517-69-7.

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Kinetics and Mechanism for Chloromercuriolactonization of Esters of γ,δ-Unsaturated Acids[1]

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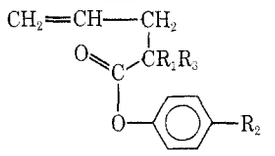
The kinetics of the reaction of phenyl allylphenylacetate (I), phenyl allyl-*p*-tolylacetate (II), phenyl *p*-methoxyphenylacetate (III), phenyl allyl-*p*-chlorophenylacetate (IV), phenyl allyl-*p*-fluorophenylacetate (V), phenyl allyl-*p*-nitrophenylacetate (VI), phenyl allylacetate (VII), *p*-tolyl allylacetate (VIII), *p*-methoxylphenyl allylacetate (IX), *p*-bromophenyl allylacetate (X), *p*-nitrophenyl allylacetate (XI), and phenyl allyldiphenylacetate (XII) with mercuric chloride have been studied in 50% aqueous ethanol. The reaction follows the expression rate = k_2[ester][$HgCl_2$]. Rate constants for the reaction are increased by electron-withdrawing substituents in the phenyl allyl para-substituted phenylacetate moiety (compounds I–VI) and by electron-donating substituents in the para-substituted allylacetate moiety (compounds VII–XI). A mechanism is postulated and discussed in terms of the kinetic data.

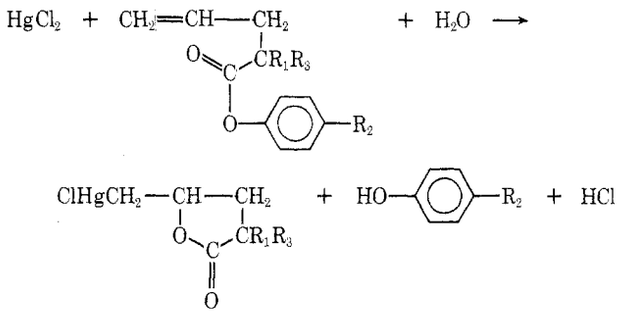
In the course of a search for new mercurials of diuretic action, we have prepared δ-chloromercuri-γ-lactones by the reaction of various allyl para-substituted acids with mercuric chloride in 50% aqueous ethanol. The structure of these chloromercurilactones were established by chemical and spectroscopic means. Aside from the pharmacological importance of these products, we were interested in studying the reaction itself to determine its kinetic expression and the effect of structural changes on its rate. Such a kinetic study was particularly interesting because of the surprisingly small amount of kinetic data available on this reaction. We have therefore prepared several phenyl esters of allyl para-substituted phenylacetate acids (compounds I to VI) and several para-substituted phenylic esters of the allylacetic acid (compounds VII to XI). See Chart I for general structure of compounds I–XII. These esters react with mercuric chloride in ethanol–water solution to give δ-chloromercuri-γ-lactones and the corre-

Chart I



Compd	R_1	R_2	R_3
I	C_6H_5	H	H
II	p-$C_6H_4CH_3$	H	H
III	p-$CH_6H_4OCH_3$	H	H
IV	p-C_6H_4Cl	H	H
V	p-C_6H_4F	H	H
VI	p-$C_6H_4NO_2$	H	H
VII	H	H	H
VIII	H	CH_3	H
IX	H	OCH_3	H
X	H	Br	H
XI	H	NO_2	H
XII	C_6H_5	H	C_6H_5

sponding phenol. The reaction rate was studied spectrometrically by observing the formation of the phenols.



Experimental Section

Ir spectra (in cm^{-1}) were measured on a Perkin-Elmer Model 337 grating spectrometer and Raman spectra on a Jarrel-Ash 25-300 spectrometer. Nmr spectra were measured on a Perkin-Elmer R-10 spectrometer. Chemical shifts (τ) in ppm were measured from an internal TMS reference. A Perkin-Elmer Model 180 instrument was used for glc analysis. In all chromatographic analysis of the esters a 3% SE-30 column was used, with nitrogen as the carrier gas. Mass spectra were recorded on a single focus Perkin-Elmer 200, operating at an ionizing potential of 70 eV. Melting points were determined on a Kofler hot stage apparatus and are uncorrected.

Preparation of Allyl Para-Substituted Phenylacetic Acids. A solution of 24 mmol of n-butyllithium (solution 2 M in hexane) was added to a solution of 24 mmol of diisopropylamine in 20 ml of THF at −5°. The acid (phenylacetic, p-tolylacetic, p-methoxyphenylacetic, p-chlorophenylacetic, p-fluorophenylacetic, or diphenylacetic), 11.3 mmol in 10 ml of THF, was added slowly. After 5 min, 5 ml of HMPT was added, and the solution stirred at 0° for 15 min. Allyl bromide (15 mmol) was then added in one portion. After stirring at room temperature for 2 hr, followed by distillation of the solvent, the residue was poured into water and extracted with ether. After removal of the ether, the crude acid was obtained (Table I).

Allyl p-nitrophenylacetic acid was synthetized as follows. Diethyl p-nitrophenylmalonate was prepared according to the method of Bourdais and Mahieu,[3] yield 47%, mp 56° (lit.[3] mp 56°). The ester was alkylated with allyl bromide in *tert*-butyl alcohol using potassium *tert*-butoxide as base to give diethyl allyl-p-nitrophenylmalonate, in 85% yield. The required acid was obtained by hydrolysis with dilute aqueous sodium hydroxide (2.8%), followed by acidification and decarboxylation: yield 73%, mp 89–90°, ν_{max} (KBr) 1710 (CO), 1525, 1340 (NO_2). *Anal.* Calcd: C, 59.72; H, 5.10. Found: C, 59.91; H, 5.21.

Preparation of Phenyl Allyl Para-Substituted Phenylacetates and Para-Substituted Phenyl Allylacetates. Phenyl allylphenylacetate (I), phenyl allylacetate (VII), p-tolylallylacetate (VIII), p-methoxyphenyl allylacetate (IX), p-bromophenyl allylacetate (X), p-nitrophenyl allylacetate (XI), and phenyl allyldiphenylacetate (XII) were prepared by heating 0.1 mol of the corresponding acid with 0.2 mol of thionyl chloride until the evolution of gases ceased. After the excess thionyl chloride was removed by distillation, 0.12 mol of the corresponding phenol was added and the mixture heated for 2–3 hr. The product was washed with cold 10% sodium hydroxide solution and water and extracted with ether; the solvent was evaporated. The residual oil was distilled to give the required ester [compound: yield, elemental analysis (calcd); boiling point; ir absorption (film)]. I: 67%; C 80.40 (80.90), H 6.66 (6.39); 127–129° (0.3 Torr); 1745, 1640, 1280–1190. VII: 52%; C 74.89 (74.85), H 7.09 (6.80); 96–100° (3 Torr); 3060, 1760, 1540, 1500, 750, 680. VIII: 64%; C 75.32 (75.76), H 7.49 (7.42); 114–118° (6–7 Torr); 3060, 1640, 1580, 1220, 840. IX: 56%; C 69.84 (69.88), H 7.04 (6.84); 103–105° (0.15 Torr); 3100, 2850, 1760, 1650–1590, 1500, 1460–1440, 1220, 1020, 840. X: 79%; C 52.21 (51.79), H 4.85 (4.35); 136–140° (0.15 Torr); 3100, 1760, 1660, 1490, 1220, 1015, 840, 520. XI: 55%; C 60.32 (59.72), H 5.04 (5.01); 130–140° (0.15 Torr); 3060, 1765, 1640, 1610–1580, 1340, 1220, 1010, 850. XII: 47%; C 84.07 (84.12), H 6.24 (6.14). Phenyl allyl-p-tolylacetate (II), phenyl allyl-p-methoxyphenylacetate (III), phenyl allyl-p-chlorophenylacetate (IV), phenyl allyl-p-fluorophenylacetate (V), and phenyl allyl-p-nitrophenylacetate (VI) were prepared by the following method. A mixture of 100 ml of DMF and 0.1 mol of thionyl chloride was heated at 40–50° for 20 min; 0.1 mol of the acid was added. The mixture was heated at 60° for 2 hr after which 0.13 mol of phenol was introduced and mixture heated for an additional 3 hr. After addition of 10% HCl solution, and extraction with ether, the combined ethereal extracts were washed with 10% HCl solution, water, and cold 10% NaOH, and then dried and the solvent evaporated. The residual oil was distilled to give the required ester [compound; yield; elemental analysis (calcd); boiling or melting point; ir absorptions]. II: 88%; C 80.90 (81.17), H 6.76 (6.81); bp 118–20° (0.8 Torr); (film) 1730, 1620, 1300–1070. III: 75%; C 68.59 (68.88), H 5.01 (5.09); bp 142–44° (0.3 Torr); (film) 1730, 1620, 1300–1050. IV: 86%; C 70.97 (71.20), H 5.21 (5.27); bp 120–122° (0.4 Torr); (film) 1748, 1630, 1250–1050. V: 86%; C 75.39 (75.54), H 5.65 (5.59); bp 120–122° (0.5 Torr); (film) 1752, 1650, 1300–1100. VI: 61%; C 68.59 (68.88), H, 5.01 (5.09); mp 45.5–46.5°; (KBr) 1730, 1530, 1340, 1250–1050.

Preparation of the δ-Chloromercuri-γ-lactones. (a) From the Corresponding Acids. Equimolar amounts of the appropriate acid and mercuric chloride were dissolved in an 80% methanol–water mixture.[4] After 6 hr the solvent was evaporated with hot air and the amorphous viscous material obtained was crystallized from ethanol, with the exception of chloromercuri-γ-valerolactone which was crystallized from chloroform–petroleum ether. The results are summarized in Table II.

(b) From the Corresponding Esters. Equimolar amounts of the appropriate esters and mercuric chloride were dissolved in an 80% methanol–water mixture. After 2 days the solvent was evaporated with hot air and the amorphous, viscous material obtained

Table I
Yield in Allylation of $R_1R_3CHCO_2H$, Employing LiDiPA as Base, in THF–HMPT Solution, and Characterization of the $CH_2{=}CHCH_2C(R_1)(R_3)CO_2H$ Formed

Registry no.	Compd	R_1	R_3	Yield, %	Mp, °C	Ir[c] ν_{max}, cm^{-1}	Nmr[e]
1575-70-8	**1**	H	C_6H_5	81	*a*	1690, 1620[d]	2.83, 4.39, 5.03, 6.47, 7.55,
51230-90-1	**2**[f]	H	p-$CH_3C_6H_4$	80	91–92	1720, 1620	2.83, 4.32, 4.96, 6.42, 7.40, 7.77
51230-91-2	**3**[f]	H	p-$CH_3OC_6H_4$	78	81–81.5	1690, 1640	2.83, 4.20, 4.90, 6.22, 6.49, 7.29
51230-92-3	**4**[f]	H	p-ClC_6H_4	83	94–95	1715, 1630	2.67, 4.42, 4.69, 6.39, 7.40
51230-93-4	**5**[f]	H	p-FC_6H_4	80	67–69	1720, 1650	2.79, 4.34, 4.92, 6.39, 7.29
6966-03-6	**6**	C_6H_5	C_6H_5	81	141–142[b]	1705, 1640	2.79, 4.49, 5.22, 6.89

[a] Bp 146–147° (15 Torr) [lit.[16] 113–117 (1 Torr)]. [b] Lit.[7] 138–140. [c] KBr. [d] Film. [e] Taken in carbon tetrachloride for compounds I and VI and in acetone-d_6 for compounds II, III, IV, and V. [f] Satisfactory combustion analytical data for C and H (±0.4%) were reported for these compounds. Ed.

Table II
Yields of the Reaction of CH_2=$CHCH_2C(R_1)(R_3)CO_2H$ and Mercuric Chloride, and Characterization of the δ-Chloromercuri-γ-lactones Formed

Registry no.	R_1	R_3	Yield, %	Mp, °C	Ir ν_{max}, cm^{-1}
51230-94-5	H	H	57	81–82[a]	1745 (CO), 530 (C–Hg)
51230-95-6	H	C_6H_5	56	172.5–173.5[b]	1740 (CO), 560 (C–Hg)
51230-96-7	H	p-$CH_3C_6H_4$	77	165–166.5[b]	1700 (CO), 553 (C–Hg), 300 (Hg–Cl)
51230-97-8	H	p-$CH_3OC_6H_4$	77	177–178.5[b]	1745 (CO), 560 (C–Hg), 300 (Hg–Cl)
51230-98-9	H	p-ClC_6H_4	80	149–150[b]	1740 (CO), 565 (C–Hg), 308 (Hg–Cl)
51271-05-7	H	p-FC_6H_4	75	180–181.5[b]	1735 (CO), 1200, 1100(C–F), 552 (C–Hg), 305 (Hg–Cl)
51230-99-0	H	p-$NO_2C_6H_4$	51	142–143[b]	1745 (CO), 1520 1350 (NO_2), 560 (C–Hg), 315 (Hg–Cl)
51231-00-6	C_6H_4	C_6H_4	82	203–204[c]	1754 (CO), 568 (C–Hg)

[a] Lit.[6] 81–82°. [b] Satisfactory combustion analytical data for C, H (±0.4%) were reported for these compounds. Ed. [c] Lit.[6] 203–204°.

from esters I, II, III, IV, V, and VI was crystallized from ethanol, and from esters VII, VIII, IX, X, and XI were crystallized from chloroform and petroleum ether (starting ester, yield): I, 40%; II, 54%; III, 51%; IV, 61%; V, 58%; VI, 33%; VII, VIII, IX, X, XI, *ca.* 10%.

Dehalomercuration of the δ-Chloromercuri-γ-lactones. The method of Brown, *et al.*,[5] was used, with the exception that the sodium borohydride (in 3 *M* sodium hydroxide solution without free alkali) was added to a THF–water solution of chloromercurilactones. The following results were obtained. (1) The reduction of δ-chloromercuri-γ-valerolactone gave allylacetic acid, identified by its ir spectrum.[6] (2) The reduction of the α-phenyl-δ-chloromercuri-γ-valerolactone gave an 85% yield of α-phenyl-γ-valerolactone; bp 154–156° (3 Torr); ir (film) 1775 (CO). *Anal.* Calcd: C, 74.97; H, 6.68. Found: C, 74.86; H, 6.79. The reduction of the α,α-diphenyl-δ-chloromercuri-γ-valerolactone gave an 80% yield of α,α-diphenyl-γ-valerolactone: mp 113–114° (lit.[7] 113–114°); ir (Nujol) 1760 (CO).

Kinetic measurements were carried out spectrophotometrically with the aid of a Zeiss PMQ II spectrometer equipped with a cell holder through which water from a thermostated bath was continuously circulated. The required reaction temperature was measured inside the cell with an accuracy of ±0.05°. All reagents were Merck R.G. grade and doubly distilled water was used throughout the work. Reagent solutions were prepared in 50% ethanol–water mixture and had the following concentrations: ester solutions, 4.0×10^{-4} *M*; mercuric chloride, 3.0×10^{-1} *M*; and sodium perchlorate, 1.0 *M*. Kinetic runs were carried out as follows. All reagents, except the ester solution, were pipetted into reaction tube, mixed, and then left in the water bath for 30 min. At zero time, a measured quantity of the ester solution was added to the mixture, which was then shaken and transferred rapidly to the reaction cell. The reaction kinetics were monitored by following the appearance of the liberated phenol at the appropriate wavelength until a constant reading was reached. In all cases a sufficient excess of mercuric chloride was used to ensure pseudo-first-order kinetic behavior. An ionic strength of 0.10 was obtained by addition of sodium perchlorate solution. Observed first-order rate constants, k_{obsd}, were evaluated from plots of log $(OD_\infty - OD_t)$ against time and the expression $k_{obsd} = 0.693/t_{1/2}$. Second-order rate constants, k_2, were determined by dividing k_{obsd} by the mercuric chloride concentration.

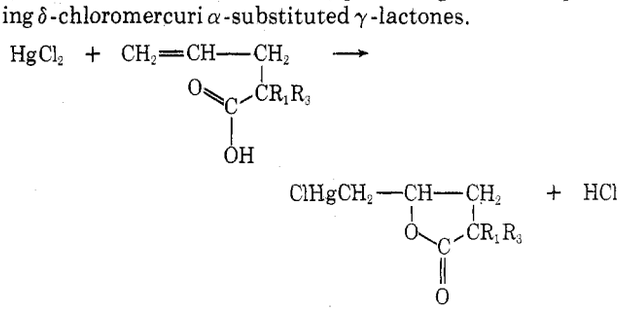
Results

Preparation of the Allylphenylacetic Acids. The usual method for preparing allylphenylacetic acids involves the hydrolysis and decarboxylation of disubstituted malonic esters. The latter compounds may be obtained by known procedures.[8]

In addition to the multistep nature of this method of synthesis, low overall yields are usually obtained (35–40%).

We have prepared several allyl para-substituted phenylacetic acids; *viz.* allylphenylacetic acid, allyl-*p*-tolylacetic acid, allyl-*p*-methoxyphenylacetic acid, allyl-*p*-chlorophenylacetic acid, and allyl-*p*-fluorophenylacetic acid as well as allyldiphenylacetic acid by direct allylation of the appropriate phenylacetic acids, employing the bulky base lithium diisopropylamide.[9] Metal amides have been used as strong bases for metalation; however, only metal alkylamides can be used with carbonyl compounds to avoid the undesirable addition of the amide ion.[10] This base results in rapid formation of the dianion of the acid at room temperature, and its use seems more advantageous in both reaction conditions and yields than the less bulky dimethyl- or diethylamine.[10] Alkylation with allyl bromide gave excellent yields of the monoalkylated acid (Table I). No dialkylated compounds could be detected by glc or nmr.

Preparation of the Chloromercurilactones. The allylphenylacetic acids, prepared as described above, were treated with mercuric chloride, producing the corresponding δ-chloromercuri α-substituted γ-lactones.



The reaction was carried out in methanol–water solution, as addition of mercuric chloride to the unsaturated acids under anhydrous conditions led to simple double bond addition, with no lactone formation.[11] It seems possible, therefore, that water participates in the transition state formed by the intramolecular attack of the carbonyl oxygen to the mercurinium ion. The chloromercurilactones were prepared in high yields (Table II).

Structure of the Lactone Ring. The ir absorption for the carbonyl group of chloromercurilactones varied between 1754 and 1735 cm^{-1}. This range corresponds to a δ-lactone (reported 1750–1735 cm^{-1})[12] rather than a γ-lactone (reported range 1780–1760 cm^{-1});[12] however, the lactones derived from γ,δ-unsaturated acids were reported to be γ-lactones.[13,14] The origin of this difference was investigated. If the observed frequencies of the lactones in the study originate from an interaction between the electropositive mercury atom and the carbonyl group, then dehalomercuration should result in a blue shift to the ν_{max} value reported for the carbonyl group in γ-lactones. This dehalomercuration was affected by sodium borohydride reduction in alkaline solution, and the results were as follows. (1) For the chloromercurilactones of allylacetic acid, it was not possible to effect reduction without regenerating the starting allylacetic acid. (2) Reduction to the chloromercurilactone derived from allylphenylacetic acid resulted in a blue shift from 1740 to 1775 cm^{-1}. (3) For allyldiphenylacetic acid, the lactone obtained by direct lactonization of the acid by concentrated sulfuric acid and by reduction of the chloromercurilactone showed the characteristic absorption of a γ-lactone (1760 cm^{-1}).

Table III
Mass Spectra of δ-Chloromercuri-α-p-chlorophenyl-γ-lactone

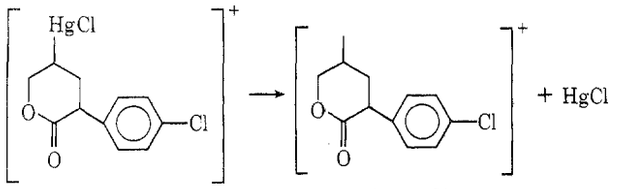
m/e	Abund., %	m/e	Abund., %	m/e	Abund., %	m/e	Abund., %
41	8	89	15	130	48	169	58
43	6	113	16	138	10	171	20
51	14	115	20	141	33	199	13
63	11	125	33	143	10	209	8
75	13	127	28	165	100	211	2
77	16	129	51	167	30		

Table IV
Second-Order Rate Constants for the Reaction of Phenyl Allyl Para-Substituted Phenylacetates and Mercuric Chloride, in 50% Ethanol–Water with Ionic Strength of 0.10

Registry no.	Substituent	$k_2 \times 10^3$, M^{-1} min^{-1} T = 25°	T = 35°	T = 45°
51231-01-7	OCH_3	8.2	18.7	38.5
51231-02-8	CH_3	7.9	18.9	43.0
51231-03-9	H	6.3	15.8	35.0
51231-04-0	F	6.5	15.4	33.4
51231-05-1	Cl		12.5	29.6
51231-06-2	NO_2		5.6	16.6

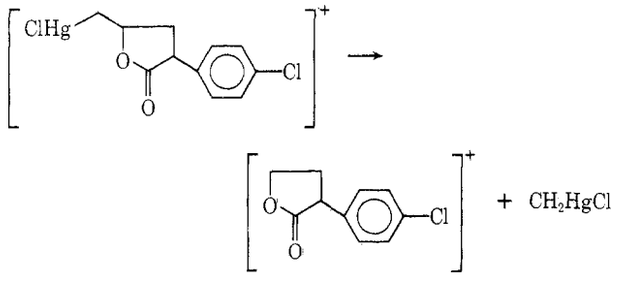
The mass spectrum of δ-chloromercuri-α-p-chlorophenyl-γ-lactone was taken in an attempt to confirm the structure of the lactone ring, since simply substituted γ- and δ-lactones give a base peak of m/e 85 and 99, respectively.[15,16] The results are shown in Table III.

However, this method of differentiation was not effective in this case because of the very low abundance of peaks with m/e 85 and 99 (2%). The parent peaks in the mass spectrum of this compound are at m/e 211 and 209, corresponding to the loss of HgCl. This loss is readily explained in the case of a δ-lactone by γ-fission.



m/e 211, 209

A similar γ-fission on the case of a γ-lactone would give rise to loss of CH_2HgCl

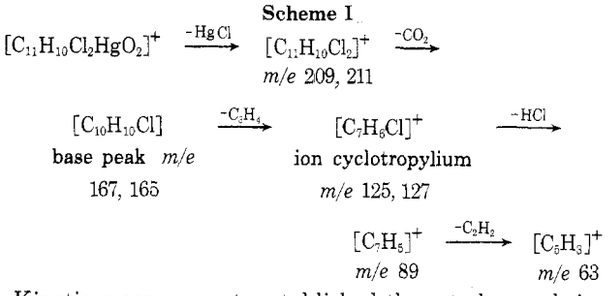


m/e 197, 195

The low abundance of peaks with m/e 197 and 195, however, does not rule out the existence of a γ-lactone since the weaker C–Hg bond should cleave more readily than C–C bond.

The ease with which the C–Hg bond breaks is demonstrated in the mass spectrum of Me_2Hg where the heat of formation, $\Delta H_f°$ of $HgCH_3^+$ (C–Hg breakage), is almost equal to that of $Hg(CH_3)_2^+$ (two-electron loss). After losing HgCl, the resulting ion loses CO_2 to produce base peaks m/e 167 and 165. Scheme I shows the prominent peaks obtained and a possible fragmentation route.

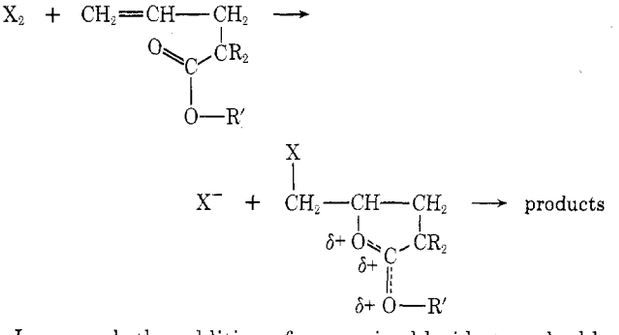
Scheme I



Kinetic measurements established the rate law as being rate = k_2[ester][$HgCl_2$]. The reaction is therefore second-order overall.

Several oxymercuration reactions have established the same kinetic behavior.[4-6,17]

Table IV shows the results obtained at different temperatures for the reaction of phenyl allyl para-substituted phenylacetates (esters I to VI) and mercuric chloride in 50% ethanol–water solution with an ionic strength 0.10. It can be seen that the presence of electron-withdrawing groups in the para position of the phenyl ring decrease the reaction rate, whereas the opposite is true with electron-donating substituents. This behavior can be explained by considering the general mechanism for the reaction of electrophilic reagents with γ,δ-unsaturated acids and esters.[20]



In general, the addition of mercuric chloride to a double bond proceeds *via* an alkenemercurinium ion, followed by a trans attack of the nucleophilic species.[18-21] This step is rapid and reversible.[21] In the chloromercuriolactonization the nucleophilic attack is made intramolecularly by the neighboring oxygen of the carbonyl group, leading to ring formation. The rate of this step is dependent on the electronic density of the carbonyl group. The presence of electron-withdrawing groups in the para position of phenyl ring decreases in the reaction rate while the presence of electron-donating groups at the same position increases the electron density of the carbonyl group and causes a rate increase.

The importance of the polar factor on chloromercuration of the γ,δ-unsaturated esters can be determined by the application of the Hammett equation. In Figure 1, values of rate constants are plotted against σ^n substituent constants.[22] A satisfactory straight line relationship is obtained, with a ρ^n value of −0.43. The rate constants are better correlated by σ^n than by σ values. This is explained by the fact that the interaction between para groups in the phenyl allyl para-substituted phenylacetates and the reaction center is believed to be purely polar since the substituents are removed by one atom from the carbonyl group. The negative sign of ρ^n indicates that the reaction rate is increased by increasing the electron density at the reaction center, *i.e.*, by electron-releasing groups. The small value of ρ^n arises from the fact that the substituents are distant from the reaction center. The activation energy E_a was determined by a least-squares analysis of a plot of log k_2 *vs.* $1/T$ (Table V).

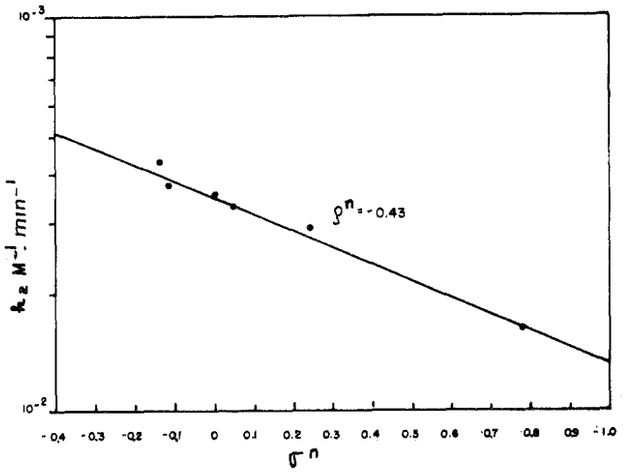


Figure 1. Logarithms of the second-order rate constants for the reaction of phenyl allyl para-substituted phenylacetates and mercuric chloride, in 50% aqueous ethanol, at 45° and an ionic strength of 0.10, plotted against σ^n substituent constants. The compounds employed and the numerical values of the rate constants are listed in Table IV.

The enthalpy of activation, ΔH^*, was obtained by subtracting RT from E_a. The entropy of activation, ΔS^*, was calculated from the formula given by Schaleger and Long.[23] It can be seen that the enthalpy of activation (ΔH^*) and the free energy of activation (ΔG^*) are higher for electron-withdrawing groups. This clearly shows the contribution of the polar effect of the substituents to the reaction rate. The values of the entropy of activation (ΔS^*) are almost constant, supporting the idea that only the polar effect is operating. The reported negative values of the entropy of activation are clearly due to the formation of a solvent shell around the ionic species in the reactions.[24]

Table VI shows the results obtained for the reaction of para-substituted phenyl allylacetates (esters VII–XI) and mercuric chloride in 50% ethanol–water solution with an ionic strength of 0.10 at 45°. It can be seen that electron-attracting groups increase the reaction rate whereas electron-releasing groups have an opposite effect. This result is the reverse of that obtained for the first series of esters

Table V
Activation Parameters for the Reaction of Phenyl Allyl Para-Substituted Phenylacetates and Mercuric Chloride, in 50% Ethanol–Water and an Ionic Strength of 0.10

Substituent	ΔE^*, kcal mol^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu	ΔG^*, kcal mol^{-1}
OCH_3	14.1	13.4	−75.1	37.3
CH_3	16.0	15.4	−74.9	39.2
H	15.5	14.9	−75.4	38.9
F	15.1	14.5	−75.4	38.5
Cl	16.8	16.2	−75.6	40.2
NO_2	21.3	20.7	−76.6	45.1

Table VI
Second-Order Rate Constants for the Reaction of Para-Substituted Phenyl Allylacetate and Mercuric Chloride in 50% Ethanol–Water and an Ionic Strength of 0.10 at 45°

Registry no.	Substituent	$k_2 \times 10^3$, M^{-1} min^{-1}
51231-07-3	OCH_3	6.2
51231-08-4	CH_3	6.9
51231-09-5	H	8.3
51231-10-8	Br	15.4
51231-11-9	NO_2	112

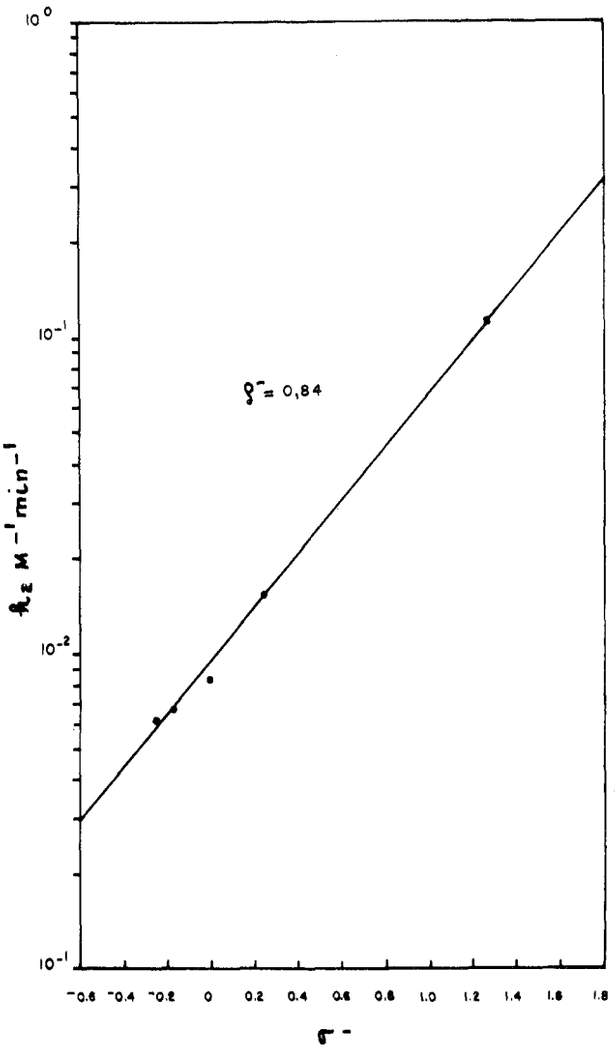


Figure 2. Logarithms of second-order rate constants for the reaction of para-substituted phenyl allylacetates and mercuric chloride, in 50% aqueous ethanol at 45° and an ionic strength of 0.10, plotted against σ^- substituent constants. The compounds employed and the numerical values of the rate constants are listed in Table VI.

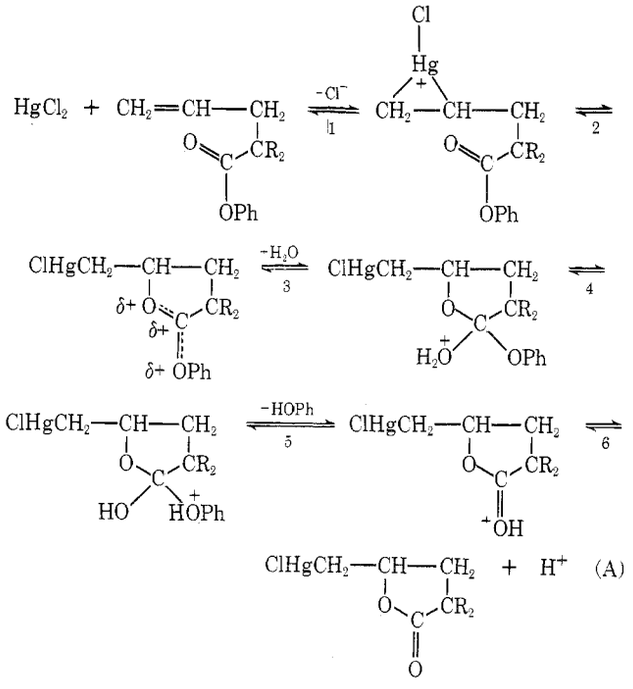
(esters I–VI) and can be explained by assuming that the reaction rate is being controlled by the ease of departure of the leaving group. Electron-attracting groups in the para-substituted phenyl allylacetates make the phenol a better leaving group, thus increasing the rate of the reaction, in accordance with the results obtained.

In Figure 2 the values of the rate constants are plotted against the σ^- substituent constants,[25] giving a ρ^- value of 0.84.

Discussion

On the basis of our results we propose mechanism A for the chloromercuriolactonization of phenyl esters of γ,δ-unsaturated esters, in ethanol–water solution. The fact that carbonyl oxygen is the one involved in the ring formation has been established previously for the same type of reaction.[26,27] Steps 1, 3, 4, and 6 are rapid.[21] The rate-determining step may be, therefore, step 2, in which intramolecular nucleophilic attack by the carbonyl oxygen leads to ring formation, or step 5, in which the phenol departs. It can be shown easily that the form of the kinetic equation obtained in either case is essentially the same.

With the para-substituted phenyl allylacetates (esters VII–XI) the rate of the reaction increases when the substituent is an electron-attracting group and decreases



when the substituent is an electron-releasing group. This suggests that the rate-determining step is the departure of the phenol (step 5), since a better leaving groups departs quicker. If the rate-determining step were the nucleophilic attack of the carbonyl oxygen on the mercurinium ion (step 2), the velocity of the reaction would decrease when the substituent is an electron-attracting group and increase when the substituent is an electron-releasing group. The experimental observations do not support the latter statement.

With the phenyl allyl para-substituted phenylacetates esters the presence of electron-withdrawing groups in the para position of the phenyl ring decreases the rate of the reaction while the presence of electron-donating groups at the same position causes an increase in the reaction rate. In these esters the leaving group remains the same, but step 2 is shifted to the right by the increase in the electron density of the carbonyl group. This further supports the postulate that the rate-determining step for the chloromercuriolactonization reaction is the loss of the substituted phenol.

Registry No.—$HgCl_2$, 7487-94-7; phenyl allyldiphenylacetate, 51231-12-0.

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Mercuric Chloride Promoted and Cobaltous Chloride Promoted Reactions of 1-Phenylethyl Chloride[1,2]

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The ionization of 1-phenylethyl chloride in anhydrous acetone is efficiently promoted by $HgCl_2$ and $CoCl_2$. The reactions measured by loss of optical activity and radiochlorine exchange provide results which are consistent with the intervention of ion-pair intermediates. In the case with $HgCl_2$ the kinetics are complicated and are consistent with the presence of two molecules of $HgCl_2$.

In the previous papers of this series we described the $HgCl_2$-promoted reactions of fairly reactive alkyl chlorides which ionized to form cations with intermediate stability such as the benzhydryl[3a] and the norbornyl[3b,c] cations. In these cases, the reactions are well behaved, showing a clean first-order dependence on the $HgCl_2$ concentration, and the importance of ion-pair intermediates was stressed. It seemed appropriate to extend this study to alkyl chlorides whose ionization reactions are more endothermic and where the cation is relatively less stable, especially since previous reports on studies with compounds of this type bring out the fact that the kinetic dependence of the reaction on $HgCl_2$ is complicated.[4-6] Thus, the hydrolysis and accompanying loss of optical activity of 1-phenylethyl chloride in aqueous acetone shows complicated kinetics and the two reactions are reported to proceed *via* different reaction pathways.[5] We now wish to present the results of a study on the $CoCl_2$-promoted and $HgCl_2$-promoted reactions of 1-phenylethyl chloride (RCl).