Stoichiometric concentration of *n*-Bu₄NCl was used, without allowance for incomplete dissociation.

Product Analysis. Reaction mixtures were extracted with pentane, and the pentane layer was washed with water (in the case of III also with dilute acid and sodium bicarbonate) and dried over MgSO₄; most of the solvent was evaporated and the remaining solution was analyzed by glc. Conditions were: for olefins IV–VII, 25% Carbowax 4000 on Chromosorb W at 160–175°; for VIII and IX, 6% SE-30 on Chromosorb W at 30°; for X, 5% Carbowax 4000 on Chromosorb W at 67°.

Samples of 1- and 3-phenylcyclopentene,[21] of norbornene and nortricyclene,[22] and of *exo*- and *endo*-2-norbornyl chloride,[23] used

for comparison, were available from earlier work. In some cases, absolute analysis of compounds VIII–IX and X was performed, using cyclohexane and decane, respectively, as internal standards, In all other cases relative amounts were determined. Relative areas were taken as the ratio of isomers in the case of olefins IV and V. as well as of VI and VII.

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Allylic Oxidation of Olefins by Mercuric Acetate[1]

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Abstract: Both the oxidation of allylbenzene by Hg(OAc)₂ and the solvolysis of cinnamylmercuric acetate give 40% α-phenylallyl acetate and 60% cinnamyl acetate. The solvolysis of crotylmercuric acetate and the oxidations of 1-and 2-olefins C$_n$H$_{2n}$ by Hg(OAc)₂ give under kinetic control exclusively the secondary allylic esters. The oxidation rate is apparently first order in the olefin–Hg(OAc)₂ adduct. Rate-determining formation of the allylic HgOAc by an S$_E'$ reaction and consecutive product-determining solvolysis of the mercurial are suggested to be involved in the allylic oxidation. The allylic isomerizations of allylic mercurials and allylic acetates are discussed.

Reaction of olefins with metal acetates M(OAc)$_n$ (M = Hg^{II},[4] Pd^{II},[5] Tl^{III},[6] Pb^{IV})[7] gives a variety of products including π complexes, adducts, diacetates, rearranged products, and allylic esters.[8] The allylic product has been visualized to arise by elimination of HM(OAc)$_{n-1}$ from the olefin–metal acetate adduct.[9] However, in the allylic oxidation by mercuric acetate[4,10]

the allylic mercuric acetates are usually the suggested oxidation intermediates. Their formation by allylic proton abstraction, followed by a radical decomposition, was initially suggested[10a] but the radical route was later discarded.[10b] They may also be formed from the adduct by the loss of HOAc.[11] Initial formation of an olefin–metal salt complex,[12] which then gives rapidly the allylic mercurial, or electrophilic attack by HgOAc⁺ with simultaneous rearrangement of the double bond,[13] both followed by C–Hg bond heterolysis, were also suggested.

Most systems oxidized (1- and 1,4-substituted cyclohexenes and cyclopentenes, other cycloolefins, 1- and 3-menthene)[14] were symmetrical and only one allylic product exists. Evidence that the cleavage of the C–Hg bond leads in these cases to a symmetrical intermediate, presumably a carbonium ion, was given by oxidation of ¹³C-[15] or ²H-[16] labeled cyclohexene or by oxidizing (+)-carvomenthene.[10a,11] The equilibration of the label or the loss of optical activity corresponds to an intermediate in which C-α and C-γ

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Table I. Distribution of Allylic Acetates from the Solvolysis of Cinnamylmercuric Acetate in AcOH at 75°

———0.013 M 1[b]———		0.03 M 1 and 0.03 M Hg(OAc)$_2$[c]	
Time, min	% 2[a]	Time, min	% 2[a]
16	37.7 ± 1.3	4	42.2 ± 0.3
27	36.9 ± 0.7	14	43.0 ± 2.0
38	36.7 ± 2.2	21	40.3 ± 2.7
55	36.0 ± 1.5	34	34.3 ± 0.5
73	32.5 ± 0.8	44	32.5 ± 0.7
		56	31.2 ± 0.7
240	37.0[d]	71	28.9 ± 0.1

[a] Per cent 2 in the allylic acetate mixture. [b] Yield of allylic acetates ca. 80%. [c] Yield of allylic acetates ca. 50%. [d] At 50°.

Table II. Solvolysis of 0.049 M 1 in AcOH at 75°

Time, sec	360	600	930	1320	1743	2550	3450	14,100
% reaction[a]	15.6	27.7	42.8	50.0	64.1	76.0	87.5	100
$10^4 k_1$, sec^{-1}	4.73	5.40	5.96	5.38	5.85	5.60	6.00	

[a] Based on the observed infinity (96% of theoretical). Ca. 2% of allylbenzene was observed. Hg was the only inorganic product.
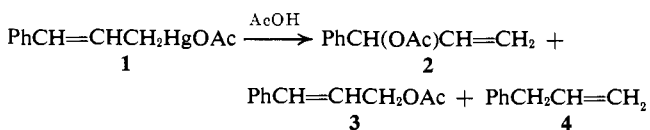
of the allylic system are identical. However, when unsymmetrical olefins were oxidized, either the rearranged allylic ester[17] or at high temperature a mixture of both allylic esters[18,19] was obtained.

Direct tests for the intermediacy of the organomercurials can be applied by studying their behavior under allylic oxidation conditions. Cinnamylmercuric acetate (1) is a possible intermediate in the Hg-(OAc)$_2$ oxidation of allylbenzene (4) and propenylbenzene (5), which gives α-phenylallyl acetate (2) and cinnamyl acetate (3).[1b] Moreover, solvolysis of crotylmercuric acetate (6) gives >99.5% of α-methylallyl acetate (7) and <0.5% of crotyl acetate (8).[20] If 6 is an intermediate in the oxidation of 1-butene (9) and possibly in that of cis-10 and trans-2-butene (11), their oxidation is predicted to give 7 almost exclusively.[1a]

The present work applies these tests and demonstrates that the allylic mercuric acetates are the most plausible intermediates in the allylic oxidation by Hg(OAc)$_2$.

Results

Acetolysis of Cinnamylmercuric Acetate. Acetolysis of 1 gives >90% of 2 and 3, 2% of 4 and traces of 5. Table I gives the distribution of the allylic acetates

$$PhCH{=}CHCH_2HgOAc \xrightarrow{AcOH} PhCH(OAc)CH{=}CH_2 +$$
$$1 \qquad\qquad\qquad\qquad\qquad 2$$

$$PhCH{=}CHCH_2OAc + PhCH_2CH{=}CH_2$$
$$3 \qquad\qquad\qquad 4$$

and shows that the percentage of 2 decreases with the progress of the reaction. This is due to isomerization of 2 to 3 which is more pronounced in the presence of

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Hg(OAc)$_2$. The kinetically controlled distribution of the allylic esters is obtained by extrapolation of the per cent 2 vs. time curves. It is 40–42% 2 and 58–60% 3, and it remains the same in the solvolyses in the presence of Hg(OAc)$_2$ or hydroquinone.

At concentrations of 1 lower than 0.005 M, metallic Hg was the inorganic product. At higher concentrations (e.g., 0.7 M), Hg$_2$(OAc)$_2$ was formed. In addition to the allylic acetates, 0.2–2.5% allylbenzene was formed, and two additional compounds with low concentrations were detected by vpc. One of them had a retention time between those of 2 and 3 (the "middle peak") and the other one had the same re-

tention time as cinnamaldehyde, which was reported to be formed in the oxidation.[21]

No cinnamyl alcohol was observed in aqueous acetic acid containing 10% (v/v) water, while few per cent of the alcohol were observed by vpc in AcOH containing 30% water (v/v).

The solvolysis in different runs was irreproducible but reasonable rate coefficients were obtained by adding preheated AcOH to 1 and using the same reaction flask. The acetolysis rate coefficients at 75° for 0.032 M and 0.049 M 1 are (6.92 ± 0.51) × 10^{-4} and (5.67 ± 0.54) × 10^{-4} sec^{-1}, respectively, and reflect the accuracy which is similar to that for other organomercurials.[22] A sample run is given in Table II.

Isomerization of 2 to 3. The equilibrium between 2 and 3 favors the primary ester which constitutes >99.5% of the equilibrium mixture at 75°. The 2 → 3 isomerization is first order in 2 and its rate coefficient k_1' increases slightly in the presence of NaOAc (Table III). In the presence of Hg(OAc)$_2$ k_1' is higher, al-

Table III. Isomerization of 2 to 3 in AcOH at 75°

2, M	Added salt	Concn, M	$10^5 k_1$, sec^{-1}
0.048			2.02 ± 0.09
0.099			2.01 ± 0.11
0.138	NaOAc	0.805	2.41 ± 0.12
0.121	Hb(OAc)$_2$	0.119	2.83 ± 0.35[a]

[a] Calculated for 40–92% reaction.

though it decreases during a run, especially at the beginning. A small amount of Hg$_2$(OAc)$_2$ and 2–3% of the "middle peak" are formed from either 2 or 3 with Hg(OAc)$_2$.
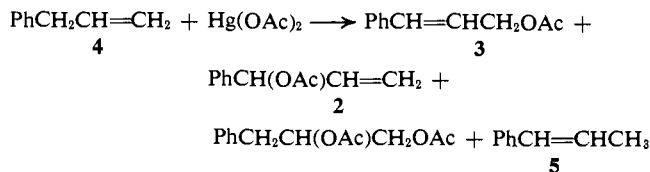
Oxidation of Allylbenzene. Hg(OAc)$_2$ (which is only moderately soluble in AcOH) dissolved rapidly with the evolution of heat on addition of allylbenzene 4. Attempts to isolate the 1:1 adduct gave only oil. The solid which separated after a long time had a different analysis from that of the adduct PhCH$_2$CH(OAc)-CH$_2$HgOAc or the dimer PhCH$_2$CH(OAc)CH$_2$HgHg-

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$CH_2CH(OAc)CH_2Ph$ which were isolated from this reaction.[21]

Oxidation of allylbenzene by $Hg(OAc)_2$ in AcOH at reflux for 50 hr gave 70% metallic Hg and 72% organic products from which cinnamyl acetate (95%), α-phenylallyl acetate (0.5%), and 1,2-diacetoxy-3-phenylpropane (2%) were isolated and identified. A compound with a retention time of *trans*-propenylbenzene (0.1%) and the "middle peak" which showed an ester carbonyl absorption in the ir were also formed. 2-Acetoxy-1-phenylpropane, the adduct of **4** with AcOH, was not formed.

$$PhCH_2CH{=}CH_2 + Hg(OAc)_2 \longrightarrow PhCH{=}CHCH_2OAc +$$
$$\underset{\textbf{4}}{} \qquad\qquad\qquad\qquad\qquad \underset{\textbf{3}}{}$$

$$PhCH(OAc)CH{=}CH_2 +$$
$$\underset{\textbf{2}}{}$$

$$PhCH_2CH(OAc)CH_2OAc + PhCH{=}CHCH_3$$
$$\underset{\textbf{5}}{}$$

The distributions of **2** and **3** in the oxidation are given in Table IV. The data represent a compromise

Table IV. Isomer Distribution in the Oxidation of Allylbenzene in AcOH at 75°

Time, min	[Allylbenzene], M	[Hg-(OAc)$_2$], M	[NaOAc], M	% **2**[a]
150	0.9	5.35		34.6 ± 0.4
150	0.46	4.92		40.0 ± 0.1
150	0.46	4.92	0.2	34.7 ± 2.1
150	0.46	4.92	0.4	36.2 ± 1.3
150	0.46	4.92	0.6	36.8 ± 1.1
113	0.31	3.20		35.3 ± 1.0
310	0.12	0.37		35.4 ± 1.1
860	1.30	2.8		26.8 ± 1.0

[a] Per cent **2** in the allylic acetate mixture.

between the need for accuracy and the use of shorter reaction times (with low yields) in order to avoid isomerization. By extrapolation, the kinetically controlled distribution is 40% **2** to 60% **3**. This distribution does not change in the presence of NaOAc. Similarly, the percentage of **2** in the allylic mixture is 14% after 45 hr with or without 0.035 M hydroquinone.

The inorganic product is Hg when **4** is in excess and $Hg_2(OAc)_2$ when $Hg(OAc)_2$ is in excess. At 1:1 concentrations Hg was usually formed, but occasionally $Hg_2(OAc)_2$ was observed at early stages of the reaction.[23]

The oxidation shows first-order kinetics in the component with the lower concentration. An increase in the concentration of the second component did not change k_1 which remains reasonably constant on changing the $[Hg(OAc)_2]:[\textbf{4}]$ ratio 67-fold (from 0.067 to 4.5). The average k_1 for 20 experiments is (10.8 ± 0.9) × 10⁻⁷ sec⁻¹. In the presence of NaOAc k_1 increases slightly, but it is practically unaffected by addition of large amounts (up to 30% v/v) of water to the AcOH (Table V). The addition of water reduces

(23) Since under the same conditions Hg is formed from 1-olefins and $Hg_2(OAc)_2$ from 2-olefins, the $Hg^{II} + Hg^o \rightleftharpoons 2Hg^I$ equilibrium seems to contribute very little at the beginning of the reaction. Formation of Hg^o from 2-olefins after long reaction times may be due to disproportionation of $Hg_2(OAc)_2$. Information on this equilibrium under our conditions is absent.

**Table V.** First-Order Rate Coefficients for the Oxidation of Allylbenzene in AcOH at 75° [a]

[Allylbenzene], $10^2 M$	[Hg(OAc)$_2$], $10^2 M$	Added substrate	$10^7 k_1$, sec⁻¹
78.0	5.24		12.0 ± 0.1
22.0	5.24		9.6 ± 0.9
8.78	3.81		12.2 ± 0.6
8.78	3.81	0.76 M NaOAc	16.6 ± 0.8
10.0	6.84		10.5 ± 1.1
8.78	7.62		12.5 ± 0.6
8.78	7.62	0.4 M NaOAc	14.9 ± 0.2
20.0	19.0		10.3 ± 1.8
1.0	0.95		10.7 ± 1.1
10.0	11.40[b]		10.8 ± 0.4
7.15	13.60[b]	0.357 M NaOAc	12.7 ± 0.3
10.0	20.5[b]		9.6 ± 1.7
1.0	4.45[b]		12.4 ± 1.4
10.0[c]	9.0		10.8 ± 1.0
10.0[d]	8.1	10% H_2O (v/v)	10.9 ± 0.7
10.0[e]	7.1	20% H_2O (v/v)	12.1 ± 1.3
10.0[f]	6.1	30% H_2O (v/v)	11.3 ± 0.9

[a] Hg is the inorganic product. [b] $Hg_2(OAc)_2$ is the inorganic product. [c] After 23 hr the percentage of **2** in **2** + **3** is 10%. [d] After 23 hr the percentage of **2** in **2** + **3** is 0.8%. Cinnamyl alcohol (3%) is formed. [e] After 23 hr the percentage of **2** in **2** + **3** is 0.5%. Cinnamyl alcohol (5%) is formed. [f] After 23 hr the percentage of **2** in **2** +**3** is 0.4%. Cinnamyl alcohol (6%) is formed.

the percentage of **2** in the acetate mixture at least tenfold, but even at 30% v/v water, the cinnamyl alcohol is only 6% of the product.

Since the kinetics fit the formation of the 1:1 adduct of **4** and $Hg(OAc)_2$, Scheme I can be used to calculate the fraction (f) of **2** in the allylic acetate mixture by comparing the calculated and the observed yields of **2** at various times. This was done by using the values $k_1' = 2.02 \times 10^{-5}$ sec⁻¹ (from Table III) and $k_1 = 10.8 \times 10^{-7}$ sec⁻¹ (from Table V), and rate equation 1 which corresponds to Scheme I. The data are

Scheme I
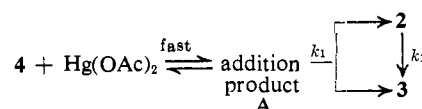
$$[2]_t/[A]_0 = f\left(\frac{k_1}{k_1' - k_1}\right)e^{-k_1't}\{e^{(k_1' - k_1)t} - 1\} \quad (1)$$

given in Table VI, and the last column shows that f decreases with the progress of the reaction but its extrapolated value is again 0.40. The decrease of f

Table VI. Calculated and Observed Isomer Distribution in the Oxidation of Allylbenzene by $Hg(OAc)_2$ in AcOH at 75°

| Time, hr	Yield of 2 + 3 (obsd)[a] %	Yield of 2 (calcd) %	% (2/f) in 2 + 3 (calcd)	% 2 in 2 + 3 (obsd)[b]	f
20	8.78	3.90	44.4	15.9 ± 0.4	0.36
44	18.35	4.52	24.6	7.9 ± 0.8	0.32
68	24.35	4.32	17.7	4.8 ± 0.3	0.27

[a] Average value from two runs. [b] Average value from four runs.

is probably due to the $Hg(OAc)_2$-catalyzed isomerization which was not taken into account in Scheme I. The maximum *yield* of **2** is calculated (by differentia-

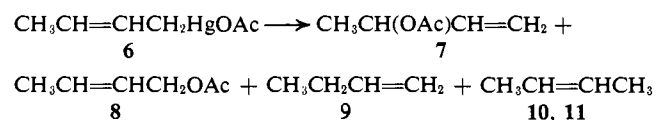tion of eq 1) to be 4.6% after 42.5 hr, in line with the data of Table VI.

Oxidation in the Presence of Acid. While 2-acetoxy-1-phenylpropane is the main product from the reaction of **4** with $HClO_4$ in AcOH, the acid also catalyzes the oxidation. After 4.5 hr in the presence of 0.14 M

$$PhCH_2CH{=}CH_2 + AcOH \xrightarrow{H^-} PhCH_2CH(OAc)CH_3$$
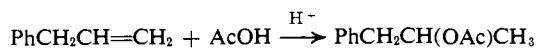
$HClO_4$, 19% of **3** is formed. However, the acid reacts further with cinnamyl acetate, giving a viscous oil, probably a telomer of **3**, with an ir spectrum similar to that of **3**.

Oxidation of Propenylbenzene. Preliminary experiments on the oxidation of propenylbenzene by Hg(OAc)₂ showed the formation of both **2** and **3** in addition to other compounds. After 4.5 hr at 75° the percentage of **2** in the allylic esters is 22% but the kinetically controlled distribution was not determined since the yields are low and the isomerization is extensive even after short reaction times.

Acetolysis of Crotylmercuric Acetate. Uncatalyzed acetolysis of 0.02–0.03 M crotylmercuric acetate gives α-methylallyl acetate (**7**), crotyl acetate (**8**), 1-butene (**9**), and cis- and trans-2-butenes (**10** and **11**). Under kinetically controlled conditions, **7** is the exclusive component (>99.5%) of the allylic acetate mixture, as reported earlier.[20] Metallic Hg is formed when **6** is <0.1 M, while at higher concentrations (e.g., 0.41 M) both Hg and Hg₂(OAc)₂ were formed. In the presence of low concentrations (e.g., 0.03 M) of Hg(OAc)₂, **7** is again 99% of **7** + **8**, but Hg₂(OAc)₂ is

$$CH_3CH{=}CHCH_2HgOAc \longrightarrow CH_3CH(OAc)CH{=}CH_2 +$$
$$\phantom{CH_3CH{=}CHCH_2HgOAc}\quad\; \mathbf{6}\mathbf{7}$$

$$CH_3CH{=}CHCH_2OAc + CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$$
$$\mathbf{8}\mathbf{9}\mathbf{10, 11}$$

the inorganic product. At higher Hg(OAc)₂ concentrations the solvolysis of **6** is very fast, the total yield of the allylic acetates is lower, and a mixture of allylic esters is obtained. When [Hg(OAc)₂]/[**6**] > 6 very few allylic acetates are formed. Control experiments showed that Hg(OAc)₂ catalyzes the **7** ⇌ **8** isomerization and also reacts with **7** and **8**. Less than 50% of allylic acetates are recovered after 24 hr at 75° from mixtures of 0.25–0.35 M allylic acetate and Hg(OAc)₂.

Oxidation of 1-Butene. 1-Butene is absorbed by a suspension of Hg(OAc)₂ in AcOH with evolution of heat and formation of a yellow color which persists until the complete dissolution of the Hg(OAc)₂. Allylic oxidation takes place slowly at 25° or at 50° giving **7** as the exclusive product (Table VII). At 75° some **8** is also formed and its percentage increases with the progress of the reaction. Extrapolation of the percentage of **7** to zero reaction time gives a kinetically controlled ratio of 98% **7** to 2% **8**. The yields of the allylic acetates were 42–50%, possibly due to their loss by reaction with Hg(OAc)₂. At 1:1 concentrations metallic Hg is the inorganic product.[23]
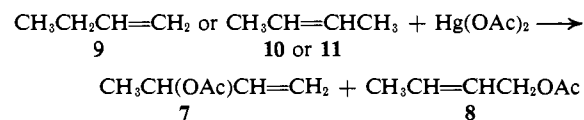
Both **10** and **11** were formed in the first run of Table VII, but the relative ratio of the three butenes was not determined. Small peaks (<1%) at retention times corresponding to that of meso-2,3-diacetoxy-butane and to a C_4 aldehyde or ketone were occasionally observed, but these were not isolated.

Table VII. Product Distribution in the Oxidation of 1-Butene and of cis- and trans-2-Butene by Hg(OAc)₂ in Dry AcOH

Butene	Concn, M	[Hg-(OAc)₂], M	Reaction time, hr	T, °C	% α-methyl-allyl acetate[a]
1-	2.22	1.97	161	25	99.7
	2.45	2.46	16	50	99.5
	1.78	1.78	65.5	50	99.7[b]
	1.85	1.85	191	50	94
			353	50	54
			19.5	75	78
	0.074	0.074	23	75	98 (98)[c]
	0.133	0.133	23	75	88 (95)[c]
trans-2-	1.81	2.01	168	23	82[d]
	2.42	1.98	39	50	90[e]
	2.42	2.42	4	75	93
	2.12	1.74	15.3	75	37.6[f]
	1.74	1.88	18	75	34.0[g]
cis-2-	3.00	1.77	96	23	97.5
	3.00	1.77	17	50	92
	2.52	1.80	16.5	50	79
	3.00	1.26	1.25	75	87.5[h]
			1.25	75	90.5[h,i]
	2.72	2.70	18	75	35.5[f]
	2.90	2.26	0.66	75	89 (99)[c]
			98	75	34
	4.21	3.50	0.2	100	74
			0.8	100	43.5
			16	100	34

[a] Percentage of the total allylic acetates. [b] At 1.6% reaction. [c] Extrapolated from the percentage of **7** vs. time curves. [d] The relative vpc area of the middle peak to those of the allylic acetates is 24%. [e] Percentage of the middle peak is 40%. [f] In the presence of 0.043 M HClO₄. [g] In the presence of 0.03 M HClO₄. [h] Middle peak ca. 5%. [i] Experiment in the presence of 0.4 M Hg₂(OAc)₂.

The kinetics of the oxidation was followed by vpc and was first order in the component with the lower concentration, i.e., in a 1:1 adduct of **9** with Hg(OAc)₂.

$$CH_3CH_2CH{=}CH_2 \text{ or } CH_3CH{=}CHCH_3 + Hg(OAc)_2 \longrightarrow$$
$$\mathbf{9}\mathbf{10 \text{ or } 11}$$

$$CH_3CH(OAc)CH{=}CH_2 + CH_3CH{=}CHCH_2OAc$$
$$\mathbf{7}\mathbf{8}$$

The calculated infinities were used since they gave no drift in k of the first 40% of the reaction, while the observed infinities gave increasing k values. The average rate coefficient is given in Table VIII.

Oxidation of cis- and trans-2-Butenes. The allylic acetate distributions from the oxidations of the two olefins are given in Table VII. The inorganic product is Hg₂(OAc)₂ except after longer reaction times when metallic Hg is formed.[23] A compound with retention time between those of **7** and **8** ("middle peak") is formed in 10–15% yield at short reaction times, but its amount decreases with time, and it is absent after long reaction times.

The rates of oxidation and of dissolution of **11** in Hg(OAc)₂ are much slower than those for **9** and **10**. The percentage of **7** has, therefore, to be determined after longer reaction times, when the isomerization is appreciable. Nevertheless, **7** constitutes >93% of the allylic mixture. The oxidation rate of cis-2-butene (based on relative yields) is comparable to that of **9** and the product distribution can be determined earlier than for **11**. At 75° **7** constitutes 99% of the initial **7** + **8** mixture, as obtained by extrapolation from per cent **7** vs. time curves.

Table VIII. Allylic Oxidation of Excess C_nH_{2n} by $Hg(OAc)_2$ in $AcOH^a$

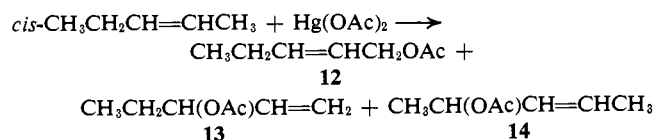| n	Olefin	T, °C	% S^b	Inorganic product^c	% S at equilibrium^b	Yield, %	$10^6 k_1$, sec^{-1} at 75°
4	1-	25	99.7	$Hg + Hg_2(OAc)_2$			
		50	99.5	Hg			
		75	94	Hg	38^d	50	1.1 ± 0.1^g
4	cis-2-	25	97.5	$Hg_2(OAc)_2$			
		50	97.5 $(99)^e$	$Hg_2(OAc)_2$			
		75	91.5 $(98)^e$	$Hg_2(OAc)_2$	$36.5,^f 35.5^d$	34.5	
4	trans-2-	50	90	$Hg_2(OAc)_2$			
		75	93.5	$Hg_2(OAc)_2$			
5	1-	50	99.6	$Hg_2(OAc)_2$	38^d		
		75	99	$Hg + Hg_2(OAc)_2$	40^d	86	1.6 ± 0.1^h
5	cis-2-	75	98.0 $(100)^e$	$Hg_2(OAc)_2$	37^f	52	
6	1-	50	97.5 $(100)^e$	Hg	34^f	90	
7	1-	75	92	Hg		95	
8	1-	50	99.6	$Hg + Hg_2(OAc)_2$			
		75	98.5	Hg	32^d	100	1.0 ± 0.2^h

^{a} Olefin concentrations 1–4 M, [Hg(OAc)$_2$] = 1–3.5 M. ^{b} Percentage of the secondary isomer in the allylic acetates mixture. ^{c} In the presence of excess olefin. With excess Hg(OAc)$_2$ the product is Hg$_2$(OAc)$_2$. ^{d} Allylic acetate distribution obtained on equilibrating mixture of allylic acetates with 0.01–0.05 M HClO$_4$. ^{e} Extrapolated from per cent S vs. time curves. ^{f} Final product distribution when the allylic oxidation was conducted with excess Hg(OAc)$_2$. ^{g} Determined by vpc. Hg(OAc)$_2$ and olefin were in 1:1 ratio. Average of four runs in the concentration range 0.07–0.74 M. ^{h} Single run followed gravimetrically. Olefin in excess. ^{i} Result of only one experiment.

The 7 ⇌ 8 Equilibrium. 7 and 8 are stable to isomerization in AcOH for 13 days at 75°. Perchloric acid or Hg(OAc)$_2$ are efficient isomerization catalysts. An equilibrium distribution of ca. 35% 7 to 65% 8, close to the reported value,[24] is obtained after long reaction times from the oxidations with excess Hg(OAc)$_2$,[25] although under these conditions Hg(OAc)$_2$ reacts slowly with 7 or 8. The same equilibrium distribution of 7 and 8 is also obtained from the perchloric acid catalyzed isomerization (Table VII).

Oxidation of Other 1-Olefins. Oxidation of the 1-olefins C_nH_{2n} (n = 5–8) showed similar behavior to that for n = 4. Hg is formed with excess olefin and Hg$_2$(OAc)$_2$ with excess Hg(OAc)$_2$. By extrapolation, the kinetically controlled percentage of the secondary ester is ≥98% (except for n = 7, where only one experiment was conducted). The yields of the allylic esters are 85–100%. The oxidations were followed gravimetrically for n = 5 and 8 and gave reasonably good k values (Table VIII). A search for 1,2-diacetate showed <0.4% for 1-hexene. "Middle peaks" of a few per cent at short reaction times, which disappeared at longer reaction times, were observed for all the olefins. The isomerization of the secondary to the primary allylic ester in the presence of Hg-(OAc)$_2$ leads to the equilibrium value after 120 hr at 75°. The equilibrium compositions were independently determined after long oxidation times in the presence of HClO$_4$ and are given in Table VIII.

Oxidation of Other 2-Olefins. Oxidation of 2-olefins other than 2-butene and 2-pentene is expected to give four allylic esters. All the four allylic esters as well as "middle peaks" were observed in the oxidation of cis-2-octene and 1-phenyl-3-pentene. Only the primary ester, 1-acetoxy-2-octene, and its allylic isomer

(24) W. G. Young and I. D. Webb, *J. Amer. Chem. Soc.*, 73, 780 (1951). At 75° at equilibrium the composition of the butenyl acetates is 38.2% α-methylallyl acetate, 10.4% cis-crotyl acetate, and 51.4% trans-crotyl acetate (H. E. Green, Ph.D. Thesis, University of California, Los Angeles, 1965).

(25) In one experiment with 10, equilibrium was apparently reached after 7.5 hr, but the percentage of 7 in the allylic mixture decreased to 26.5 and 14.5% after 23 and 26 hr (ca. 5% reaction), respectively. At >15% reaction the equilibrium distribution is again obtained. This may be due to a preferential reaction of one ester with the slight excess of Hg(OAc)$_2$ present.

3-acetoxy-1-octene, were isolated from the former oxidation, and only 1-acetoxy-5-phenyl-2-pentene from the latter oxidation. A one-point experiment gave $k = 8 \times 10^{-7}$ sec^{-1} for the oxidation of 1-phenyl-3-pentene. From the oxidation of cis-2-pentene, three allylic acetates 12, 13, and 14 and Hg$_2$(OAc)$_2$ were isolated, and two "middle peaks" were observed. The primary ester, 1-acetoxy-2-pentene 12 is only 1.2% of the 12–13 pair after 50 min. Later, its amount approaches the equilibrium value, but extrapolation shows that under kinetic control, the secondary ester 3-acetoxy-1-pentene (13) is formed exclusively. The ratio of 14 to (13 + 12) is 1:4 during most of the reac-

$$cis\text{-}CH_3CH_2CH{=}CHCH_3 + Hg(OAc)_2 \longrightarrow$$
$$CH_3CH_2CH{=}CHCH_2OAc +$$
$$\textbf{12}$$
$$CH_3CH_2CH(OAc)CH{=}CH_2 + CH_3CH(OAc)CH{=}CHCH_3$$
$$\textbf{13} \qquad\qquad\qquad \textbf{14}$$

tion, but it increases to 1:3 at longer reaction times. The oxidation rate is close to that of 1-pentene and from one-point experiment $k_1 = 1.7 \times 10^{-6}$ sec^{-1}.

Identification of the Allylic Esters. On XF-1150 column the retention times of the secondary esters are much shorter than those of the primary ones. The secondary esters are characterized by bands at 1631 and ca. 1420 cm^{-1}, and the primary esters by band at ca. 1660 cm^{-1}. The nmr spectra of the secondary esters show a complex multiplet for the three vinylic and the one methine proton. For the primary esters a two-hydrogen multiplet corresponds to the vinylic protons, while a simpler two-hydrogen multiplet is ascribed to the allylic protons α to the acetoxy group.

Discussion

The similar distribution of the allylic acetates in the oxidation of allylbenzene and in the solvolysis of cinnamylmercuric acetate which differs from the similar distribution of allylic esters in the oxidation of 1-butene and in the solvolysis of crotylmercuric acetate argues strongly for allylic mercuric acetate as the oxidation intermediates in both systems. This conclusion gains support from the exclusive formation of the secondary acetate in the oxidation of 1-butene, which
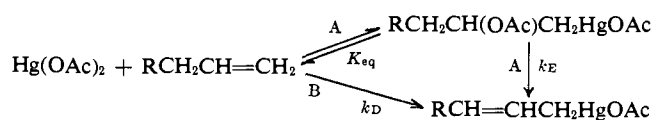
is inconsistent with an ionic or a radical mechanism. The unique and identical product distribution in the oxidation of both 1- and 2-olefins suggests that in the oxidation of the 2-olefins the rearrangement of the initially formed secondary allylic mercuric acetate to its primary isomer precedes the solvolysis of the organomercurial.

The solvolyses of cinnamyl- and crotylmercuric acetates are 580- and 31-fold faster than the oxidations of allylbenzene and 1-butene, respectively. Hence, allylic mercurials do not accumulate and the reaction can be discussed in terms of three different steps: (a) rate-determining formation of the allylic mercuric acetate intermediates, (b) product-forming solvolysis of the allylic mercurials, and (c) further reactions of the allylic esters, leading to the equilibrium distribution.

Formation of the Allylic Mercuric Acetate. The yellow color which persists until the complete dissolution of the olefin in the $Hg(OAc)_2$ is probably due to the formation of a π complex[26a] or a mercurinium ion, which was recently observed.[26b] The fast dissolution and decoloration show that under the allylic oxidation conditions the acetoxymercuration is rapid and relatively complete with 1-olefins. However, the formation of $Hg_2(OAc)_2$ in the oxidation of 2-olefins and the enhanced isomerizations in these oxidations are two phenomena associated with the presence of $Hg(OAc)_2$. More "free" $Hg(OAc)_2$ is thus present in mixtures of $Hg(OAc)_2$ with 2- than with 1-olefins, i.e., the acetoxymercuration is less complete with 2-olefins. This is in line with the order of disappearance of the yellow colors: 1-olefin > cis-2-olefin > trans-2-olefin, which also parallels the order of stability of the Ag^+ complexes of these olefins.[27]

The first-order kinetics in the 1:1 adduct of the two reactants in the oxidation of 1-olefins is consistent with two routes (Scheme II). In route A the

Scheme II

$$Hg(OAc)_2 + RCH_2CH{=}CH_2 \underset{B}{\overset{A}{\rightleftarrows}} \overset{K_{eq}}{\underset{k_D}{\rightleftarrows}} \begin{array}{c} \overset{A}{\longrightarrow} RCH_2CH(OAc)CH_2HgOAc \\ A \downarrow k_E \\ RCH{=}CHCH_2HgOAc \end{array}$$

elimination of AcOH from the adduct is rate determining, with $k_1 = k_E$. In route B, which is an SE mechanism, the reaction is between "free" olefin and "free" $Hg(OAc)_2$ both in equilibrium with the adduct for which K_{eq} is high, and $k_1 = k_D/K_{eq}$.

Although route A had been implied,[11] route B conforms better to the following facts. (a) k_1 is too high for E2 or E1 elimination of AcOH from molecules no more activated than the adducts. (b) The oxidation rates of 1-butene, 1-pentene, 1-octene, and allylbenzene are very close. In route A the allylbenzene adduct should be more reactive than the other ones by the E2 mechanism due to the stabilization of the developing double bond by the phenyl substituent.[28] (c) k_E should be sensitive to the presence of bases such as NaOAc, contrary to what was found.

(26) (a) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, 61, 3102 (1939); (b) G. A. Olah and P. R. Clifford, *ibid.*, 93, 1261, 3230 (1971).

(27) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer and R. S. Irwin, *ibid.*, 87, 1827 (1965).

(28) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, 1, 225 (1962); *Surv. Progr. Chem.*, 5, 53 (1969).

The insensitivity of the reaction rate to salt and solvent effects argues against the formation of a free carbonium ion. The reaction may be an SEi' (**15**) or $SE2'$ (**16**), both of which are the microscopic reversals of the SEi' and the $SE2'$ reactions of acids with butenylmercuric halides,[20] or it may be an ion-pair variant, **17**. With a distance of 2.48 Å between the α- and the γ- carbons of the allylic system and a Hg–O bond of 2.10 Å (based on the covalent radii)[29] little stretching of the Hg–O bond is sufficient to bring the mercury and the α-carbon and simultaneously the acetoxy oxygen and the γ-hydrogen to bonding distances. The acetate of the neutral $Hg(OAc)_2$ or of the ion pair thus serves as a "built in" base for the expulsion of the γ-hydrogen (e.g., in **17**), explaining

15   16

17
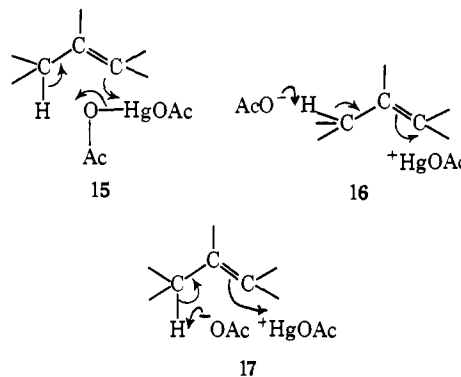
the insensitivity of the rates to the presence of the basic NaOAc.

Since the covalent $HgCl_2$ is a rather inefficient oxidant for allylbenzene[30] while the ionic mercuric perchlorate (from $Hg(OAc)_2$ and $HClO_4$) is highly reactive, an $AcOHg^+{-}OAc$ ion pair is a likely electrophile. It is known that $Hg(OAc)_2$ is only slightly dissociated in AcOH,[21] and this is consistent with the absence of common ion rate depression in the oxidation at AcO^- concentrations as high as 0.76 M.

The involvement of the γ-hydrogen bond cleavage in the rate-determining step explains the predominance of the acetates derived from attack of $HgOAc^+$ on C-3 of cis-2-pentene over that derived from attack on C-2. If only bond formation is significant, the electrophilic reaction at C-2 will predominate as judged by the more negative σ^* value of the ethyl compared with the methyl substituent.[31] However, this effect is more than compensated by the higher acidity of the methyl compared with the methylene hydrogen,[32] leading to preference of transition state **19** over **18**.

18   19
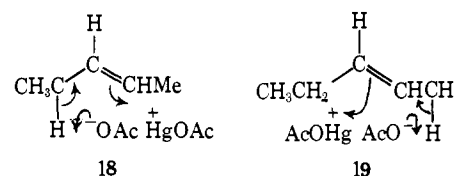
Solvolysis and Behavior of the Allylic Mercuric Acetates. Primary allylic mercuric acetates are the first

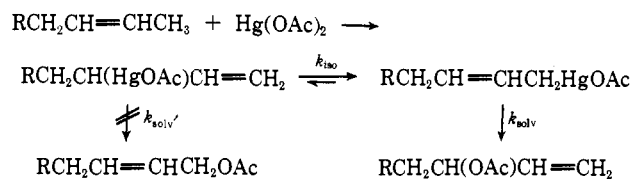(29) T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1955, p 135.

(30) Z. Rappoport, S. Winstein, and W. G. Young, unpublished results.

(31) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(32) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1.

intermediates formed in the S_E reaction of 1-olefins, and secondary allylic mercuric acetates are formed initially from 2-olefins. In analogy with the formation of rearranged allylic acetates in the solvolysis of **6**, direct solvolysis of the secondary mercurials should give exclusively the primary allylic acetate, or a mixture of primary and secondary esters if the solvolysis is *via* a carbonium ion. It is highly unlikely that the exclusive formation of the secondary ester from the 2-butenes and from *cis*-2-pentene is by any mechanism not including the primary allylic mercurial formed in the oxidation of 1-olefins. The structure of allylic MgX,[33a] allylic Li,[33b] and allylic $PdCl$ (in $DMSO$)[33c] as well as that of allylic mercuric halides in the presence of Hg salts[20] is consistent (by nmr evidence) with a rapidly equilibrating pair of σ-allyl species. Nmr shows that the equilibrium is overwhelmingly on the primary side with the butenyl and the cinnamyl systems, as is the case with the allylic Grignard reagents.[33a] The formation of $Hg_2(OAc)_2$ in the oxidation of the 2-olefins shows that there is sufficient "free" $Hg(OAc)_2$ to isomerize the secondary allylic acetate to the primary allylic acetate. Apparently, such an isomerization takes place (Scheme III). From the product

Scheme III

$$RCH_2CH=CHCH_3 + Hg(OAc)_2 \longrightarrow$$

$$RCH_2CH(HgOAc)CH=CH_2 \overset{k_{iso}}{\rightleftharpoons} RCH_2CH=CHCH_2HgOAc$$

$$\downarrow k_{solv}' \qquad\qquad\qquad \downarrow k_{solv}$$

$$RCH_2CH=CHCH_2OAc \qquad RCH_2CH(OAc)CH=CH_2$$

distribution in the solvolysis of **6** and the percentage of **8** obtained under kinetically controlled conditions we estimate that at most 1% of **8** is formed directly from the solvolysis of the secondary mercurial. Hence $k_{iso} \gg k_{solv}'$ and the isomerization is very rapid, especially since $k_{solv}' > k_{solv}$.

The details of the mechanism of the allylic mercurial rearrangement *via* transition-state **20** as well as the S_{Ni} (**21**) nature of the solvolysis of crotylmercuric acetate were discussed earlier.[20] Formation of $Hg_2(OAc)_2$ with $Hg(OAc)_2$ without affecting the allylic ester distribution can be depicted as in transition-state **22**, which is the "assisted" analog of **20**.

In the series allyl–crotyl–cinnamylmercuric acetate the reactivity ratios are 1:4:80; the percentages of olefin formed are 80:16:1 and the allylic acetate ratio
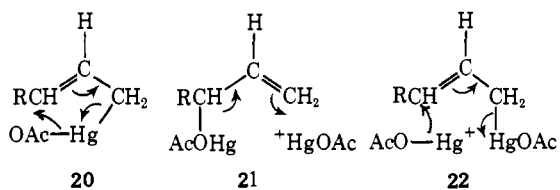

changes from >99.5% secondary for **6** to *ca.* 40% secondary for **1**. The products from **6** and the small rate difference compared with allylmercuric acetate suggest a nonionic cyclic mechanism for the demercuration of **6**.[20] The solvolysis of **1** differs, however, from that of

6, since the products from **1** may also arise by a carbonium ion or a radical mechanism. The insensitivity of the rates and the products to hydroquinone, the product distribution, and the **6/1** rate ratio are more consistent with an ionic mechanism. The rate ratios are however much lower than for the solvolysis of cinnamyl–crotyl–allyl chlorides in 50% ethanol (8000:95:1)[34] or from the ratios predicted (10^4 per methyl group) for a fully developed carbonium ion.[35] This ratio and the absence of appreciable solvent and salt effects are in line with an ion-pair mechanism for the solvolysis of **1**. Cinnamyl alcohol may be formed from the ion pair, since some allylic solvolysis products arise from ion pairs.[36]

The allylic acetate distribution is very close to that obtained in the AgOAc-catalyzed solvolysis of cinnamyl chloride and a common intermediate in both reactions is possible.[37] However, the formation under kinetic control of more primary than secondary ester is difficult to explain in terms of a free carbonium ion.[38] A model of **1** shows that due to the long C–Hg and Hg–O bonds there are many conformations in which the acetate oxygen is closer to the α- than to the γ-carbon. The product distribution is therefore not inconsistent with an ion-pair intermediate (Scheme IV).

Scheme IV
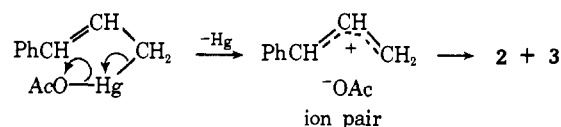
Allylic Ester Isomerizations. At equilibrium, cinnamyl acetate predominates (>99.5%) in the allylic mixture due to the phenyl–double bond conjugation. For the other acetates, the primary–secondary ratio at equilibrium is *ca.* 1.5. The kinetically and thermodynamically determined allylic ester distributions from the oxidation differ markedly and unassisted, $Hg(OAc)_2$-assisted, and acid-catalyzed isomerizations follow the solvolysis.

The unassisted isomerization observed for **2** may be an ionic process, since **7** is unreactive. It is not an S_N2' since it is insensitive to the concentration of NaOAc. The $HClO_4$-catalyzed isomerization is probably an addition–elimination process. The $Hg(OAc)_2$-catalyzed isomerization is likely to be a non-Markovnikov acetoxymercuration followed by deacetoxymercuration involving the original acetoxy group. The reaction is reminiscent of the mercuric salt catalyzed transesterification of vinyl esters with carboxylic acids,[39] or the related transetherification for which a similar mechanism has been suggested.[40]

(33) (a) J. E. Nordlander and J. D. Roberts, *J. Amer. Chem. Soc.*, 81, 1769 (1959); J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, 83, 494 (1961); (b) C. S. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *ibid.*, 83, 1306 (1961); (c) J. C. W. Chien and H. C. Dehm, *Chem. Ind. (London)*, 745 (1961).

(34) C. A. Vernon, *J. Chem. Soc.*, 423, 4462 (1954).

(35) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; S. Winstein, E. Grunwald and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951).
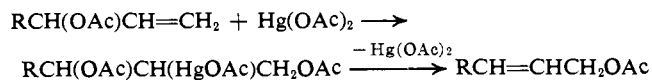
(36) W. G. Young, S. Winstein, and H. L. Goering, *ibid.*, 73, 1958 (1951).

(37) J. Meisenheimer and J. Link, *Justus Liebigs Ann. Chem.*, 479, 211 (1930).

(38) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 56, 753 (1956); S. Patai, Ed., "The Chemistry of Alkenes," Interscience, London, 1964, Chapter 10.

(39) R. L. Adelman, *J. Org. Chem.*, 14, 1057 (1949); G. Slincks and G. Smets, *Tetrahedron*, 22, 3162 (1966), and references therein. See also J. E. Byrd and J. Halpern, *Chem. Commun.*, 1332 (1970).

(40) R. L. Adelman, *J. Amer. Chem. Soc.*, 77, 1669 (1955); W. H. Watanabe and L. E. Conlon, *ibid.*, 79, 2828 (1957).

RCH(OAc)CH=CH₂ + Hg(OAc)₂ ⟶

$$RCH(OAc)CH(HgOAc)CH_2OAc \xrightarrow{-Hg(OAc)_2} RCH=CHCH_2OAc$$

Formation of Nonallylic Products in Oxidation. Allylbenzene and the butenes are formed, respectively, in the solvolyses of 1 and 6, and are part of the oxidation-solvolysis reaction. The 2% of 1,2-diacetate in the oxidation of 4 is probably formed by a neighboring acetoxy-assisted deacetoxymercuration, and it is remarkable that the decomposition of the adduct is preferred to its solvolysis. The ratio of the two processes is highly sensitive to the nature of the C-metal bond. Diacetates are the main products in the Tl(OAc)₃[41] and are also formed in the Pb(OAc)₄ oxidations of the same olefins.[41]

The "middle peaks," which by ir are esters, have the same retention times as the enol acetates which are the main oxidation products of the olefins with Pd(OAc)₂.[5] They are probably derived in a similar way by the elimination of HHgOAc from the adducts. The other compounds observed which are aldehydes or ketones (by ir and vpc) are probably formed from the hydrolysis of these enol acetates.

Synthetic Applications. The data of Table VIII suggest high utility for the oxidation reaction with Hg(OAc)₂ which gives high oxidation yields, easy separation from inorganic products, low amount of side products, and the less stable allylic ester. Terminal olefins are preferred as substrates and excess Hg(OAc)₂ should be avoided unless a mixture of the allylic esters is required. The Hg(OAc)₂ oxidation gives much more allylic esters than the Pd, Pb or Tl acetates oxidations and is reminiscent of the oxidation with peresters in the presence of cupric salts.[42] With aryl-substituted olefins, mixtures of allylic products are expected.

Implications to Other Oxidations. Our mechanism has implications for previous mechanistic tests based on symmetry arguments. The loss of optical activity in the Hg(OAc)₂ oxidation of (+)-carvomenthene[10a,11] or the complete isotopic scrambling of the two ends of the allylic system in the oxidation of cyclohexene[15,16] was taken as evidence for the intermediacy of a symmetrical intermediate. The same result would be obtained from a "switching" pair of secondary allylic mercuric acetates if the "switching" is faster than the solvolysis. Carbonium ions may be or may not be formed at a later stage. However, the involvement of one intermediate compared with a pair of rapidly equilibrating ones should always be considered.

Cyclohexenylmercuric acetate was ruled out by Wolfe[16] as an intermediate in the allylic oxidation of 3,3,6,6-tetradeuteriocyclohexene since he anticipated, but did not find, the incorporation of hydrogen from the solvent in the olefin formed by demercuration of an intermediate allylic mercurial. From our data, less olefin is formed with the increase in the reactivity of the organomercurial. Since the secondary cyclohexenylmercuric acetate is expected to be more reactive than 6, the amount of cyclohexene from its solvolysis is predicted to be low, invalidating Wolfe's argument.

Metal salt catalyzed postisomerization of the allylic esters should also be taken into account. We believe that the low yield of 2 reported[21] in the oxidation of 4 is due to this reason. Although the kinetically controlled percentage of 2 in the allylic esters mixture is 40%, the calculation of Table V showed that the maximum *yield* of this ester will be obtained after 17.5 hr and will be 4.6%.

Finally, the unique product distribution from the solvolysis of 6 suggests that similar distributions from other metal salt oxidations may be due to an allylic metal salt intermediate. The allylic oxidation of olefins by peresters in the presence of cupric salts[42] gives predominantly 7 from the butenes. One explanation[42c] involving ligand transfer and allylic cupric salt intermediates is supported by the analogy to the behavior of our compounds.

Experimental Section

α-Phenylallyl acetate, bp 92° (2 mm), n^{25}D 1.509, cinnamyl acetate, bp 113° (2.4 mm), α-methylallyl acetate, bp 111°, crotyl acetate, bp 131°, cinnamylmercuric acetate, mp 98°, and crotylmercuric acetate, mp 78°, were prepared as described elsewhere.[43] The liquid esters were >99.5% pure by vpc. Allylbenzene was prepared from allyl bromide and phenylmagnesium bromide,[44] and was >99.9% pure: bp 157° (735 mm) (lit.[45] 156–157° (760 mm)); n^{27}D 1.508 (lit.[45] 1.515). Propenylbenzene[45] was purified by vpc on a saturated AgNO₃ column. 1-Butene, cis- and trans-2-butene, and 1-pentene (Matheson) were >99% pure. 1-Octene (Matheson) was purified by distillation. Hg(OAc)₂ (Baker Analyzed) was crystallized from 20% AcOH–80% water and dried at 110° to constant weight. Acetic acid was prepared by fractionation from the calculated amount of acetic anhydride after reflux for 24 hr. The acid, bp 117° (753 mm), was dry to Karl Fischer reagent.

1,2-Diacetoxy-3-phenylpropane. 1,2-Dibromo-3-phenylpropane[46] (15 g) and silver acetate (20 g) were refluxed in acetic acid (150 ml) for 20.5 hr. The mixture was poured into water (500 ml) and extracted twice with methylene chloride (200 ml), the solvent was dried (Na₂SO₄) and removed *in vacuo*, and the residue was distilled at 156° (8 mm), giving 12.6 g (98%) of organic material containing 4% cinnamyl acetate and *ca.* 95% 1,2-diacetoxy-3-phenylpropane[47] which was purified by vpc: n^{25}D 1.4900; nmr δ 2.03 (6 H, 2 s, 2COMe), 2.98 (2 H, d, J = 7.2 Hz, benzyl), 4.23 (2 H, octet, terminal CH₂), 5.41 (1 H, octet, CH), 7.50 (5 H, s, Ph). The octet splitting remains the same at 0 and 40°. The ir is very similar to that of cinnamyl acetate. *Anal.* Calcd for C₁₃H₁₆O₄: C, 66.08; H, 6.83 Found: C, 66.01; H, 6.56.

Stabilities of Starting Materials and Products. Solutions of 0.27 M 7 and 0.61 M 8 in AcOH were kept for 13 days at 75°. The recovered esters were >99% pure. 4 (1 M) in AcOH was left for 97 hr at 75° with and without 1.48 M NaOAc. The recovered material was only 4, although 0.01% of 5 could be detected. Diethyl adipate (the vpc standard) was recovered unchanged from a 1:2 mixture with Hg(OAc)₂ at 75° for 1 week. 2 and 3 were stable on the XF-1150 column under the analysis conditions. 1,2-Diacetoxy-3-phenylpropane (189 mg) and Hg(OAc)₂ (725 mg) in AcOH (10 ml) were kept for 74 hr at 75°. After work-up, >99.5% of the diacetate was recovered unchanged.

Reactions of the Allylic Esters in the Presence of Hg(OAc)₂. 7 (0.24)M and Hg(OAc)₂ (0.29 M) were kept for 23 hr in acetic acid at 75°. Only 38% of the allylic esters was recovered with a composition of 40% 7 and 60% 8. When 0.2 M 7 and 0.2 M Hg(OAc)₂ in AcOH were kept for 5 hr at 50°, the recovered ester was 22% 8.

8 (0.29 M) and Hg(OAc)₂ (0.37 M) in AcOH were kept for 23 hr at 75°. Only 48% of the allylic esters was recovered with a composition of 21% 7 and 79% 8.

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Table IX. Vpc Data on the XF-1150 Column[a]

Compound	Column length, m	Column T, °C	Injector T, °C	He pressure, psi	Retention time, min
MeCH=CHCH₂OAc	3	65	145	10	16.9
MeCH(OAc)CH=CH₂	3	65	145	10	8.1
EtCH=CHCH₂OAc	3	74	160	12	18.8
EtCH(OAc)CH=CH₂	3	74	160	12	9.8
MeCH=CHCH(OAc)Me	3	74	160	12	8.6
PrCH=CHCH₂OAc	2	66	150	10	21.6
PrCH(OAc)CH=CH₂	2	66	150	10	10.0
BuCH=CHCH₂OAc	2	80	180	10	28.0
BuCH(OAc)CH=CH₂	2	80	180	10	13.5
n-C₅H₁₁CH=CHCH₂OAc	3	133	187	16	20.5
n-C₅H₁₁CH(OAc)CH=CH₂	3	133	187	16	10.1
PhCH=CHCH₂OAc[b]	2	155	190	15	20.0
PhCH(OAc)CH=CH₂[b]	2	155	190	15	6.0
PhCH₂CH₂CH=CHCH₂OAc	2	154	195	15	40.0

[a] On 60-80 Chromosorb W. [b] 25% column. Other retention times (in minutes); allylbenzene, 1.2; 2-acetoxy-1-phenylpropane, 6.4; diethyl adipate, 10.0; 1,2-diacetoxy-3-phenylpropane, 60.

Table X. Allylic Acetates from the Oxidation of Olefins by Hg(OAc)₂ in Acetic Acid

Allylic acetate	Formula	Anal. Calcd C	Calcd H	Obsd C	Obsd H	Ir (cm⁻¹)[a] in CCl₄	Nmr (in δ units) in CCl₄ Me	AcO	CH₂O	CH=CH
MeCH=CHCH₂OAc[b]	C₆H₁₀O₂	63.13	8.83	63.17	8.82	1722 (s), 1662 (w)	1.68 (d)	1.90 (s)	4.32 (d)	5.5 (m)
MeCH(OAc)CH=CH₂[c]	C₆H₁₀O₂	63.13	8.83	63.00	9.05	1722 (s), 1631 (m), 1420 (m)	1.24 (d)	1.95 (s)	4.90–6.00 (m)	
EtCH=CHCH₂OAc[b]	C₇H₁₂O₂	65.59	9.44	65.38	9.50	1722 (s), 1660 (w)	1.01 (t)	1.97 (s)	4.42 (d)	5.57 (m)
EtCH(OAc)CH=CH₂[b]	C₇H₁₂O₂	65.59	9.44	65.79	9.39	1722 (s), 1631 (m), 1420 (m)	0.97 (t)[d]	1.97 (s)	4.90–5.75 (m)	
PrCH=CHCH₂OAc[b]	C₈H₁₄O₂	67.57	9.92	67.42	10.03	1722 (s), 1655 (w)	0.91 (t)[d]	1.95 (s)	4.43 (q)	5.5 (m)
PrCH(OAc)CH=CH₂[b]	C₈H₁₄O₂	67.57	9.92	67.71	9.72	1722 (s), 1630 (w), 1410 (m)	0.93 (t)[d]	1.97 (s)	4.90–5.80 (m)	
BuCH=CHCH₂OAc[b]	C₉H₁₆O₂	69.19	10.32	69.16	10.28	1722 (s), 1655 (w)	0.91 (t)[d]	1.97 (s)	4.40 (q)	5.5 (m)
BuCH(OAc)CH=CH₂[b]	C₉H₁₆O₂	69.19	10.32	69.12	10.32	1722 (s), 1631 (w), 1418 (m)	0.91 (t)[d]	1.98 (s)	4.97–6.00 (m)	
n-C₅H₁₁CH=CHCH₂OAc[c]	C₁₀H₁₈O₂	70.54	10.66	70.49	10.67	1722 (s), 1675 (m), 1660 (w)	0.90 (t)[d]	1.96 (s)	4.40 (d)	5.6 (m)
n-C₅H₁₁CH(OAc)CH=CH₂[b]	C₁₀H₁₈O₂	70.54	10.66	70.68	10.88	1722 (s), 1631 (m), 1420 (m)	0.91 (t)[d]	1.97 (s)	4.90–5.90 (m)	
PhCH₂CH₂CH=CHCH₂OAc	C₁₂H₁₆O₂	76.44	7.89	76.41	8.03	1722 (s), 1630 (m), 1440 (s)	e	1.95 (s)	4.40 (d)	5.64 (q)

[a] Only characteristic bands or those differentiating between the primary and secondary esters are given. [b] From the oxidation of the terminal olefin. [c] From the oxidation of the 2-olefin. [d] A multiplet for the aliphatic protons is observed at δ 1.3–1.6. [e] CH₂ protons are multiplets at δ 2.58; Ph is a singlet at δ 7.15.

2 (0.06 M) and Hg(OAc)₂ (0.2 M) in AcOH were kept at 75° for 24 hr. A few crystals of Hg₂(OAc)₂ were formed. The composition of the recovered ester was 97.2% **3** and 2.8% "middle peak."

3 (0.2 M) and Hg(OAc)₂ (0.32 M) in AcOH gave, after 25 hr at 75°, a few needles of Hg₂(OAc)₂. The product was 98.2% **3** and 1.8% "middle peak." Reaction for 90 hr gave Hg, Hg₂(OAc)₂, "middle peak," and few additional organic compounds (by vpc) which were not characterized.

Oxidation of 4 in AcOH. 4 (5.2 g) and Hg(OAc)₂ (20.8 g) in AcOH (100 ml) were refluxed for 50 hr. Hg (9.1 g, 70%) was precipitated. The mixture was poured into water, extracted twice with pentane (100 ml), washed (water, aqueous NaHCO₃), and dried (Na₂SO₄). The solvent was evaporated and the remainder distilled at 128° (5 mm) giving 5.35 g (72%) of organic product, 95% of which is **3** (by vpc). Chromatography on silica gel (200 g) gave 4.8 g (61%) of **3**: nmr (CCl₄) δ 1.93 (3 H, s, Me), 4.60 (2 H, d, J = 5 Hz, CH₂), 6.3–6.4 (2 H, m, CH=CH), and 7.2 (5 H, broad s, Ph); ir (CCl₄) 1770 cm⁻¹. Both ir and nmr are identical with those of an authentic sample.

Anal. Calcd for C₁₁H₁₂O₂: C, 74.97; H, 6.86. Found: C, 75.05; H, 6.85.

A few milligrams of the fraction with a retention time corresponding to 1,2-diacetoxy-3-phenylpropane were collected. The ir (C=O at 1710 cm⁻¹) was identical with that of an authentic 1,2-diacetoxy-3-phenylpropane.

2 was collected from the early points of several kinetic runs. It had ir (C=O at 1725 cm⁻¹) and retention time (on two vpc columns) identical with those of the authentic sample: nmr (CCl₄) 2.00 (3 H, s, Me), ca. 5.2 (2 H, m, =CH₂), ca. 6.0 (2 H, q, CH=CH), 7.27 (5 H, s, Ph).

Attempts to Prepare the 4-Hg(OAc)₂ Adduct. On mixing 4 (4.75 g) and Hg(OAc)₂ (13.3 g) in AcOH (20 ml) heat was evolved. Stirring continued for 15 min and when all the Hg(OAc)₂ was dissolved the mixture was poured into ice-water and extracted with methylene chloride (200 ml) and the solvent was evaporated. The remaining oil could not be crystallized (benzene-petroleum ether, AcOH, aqueous acetone) or solidify on chromatography (silica gel). After 2 months at room temperature a solid separated, but the analysis (*Anal.* Found: C, 19.57; H, 2.04; Hg, 64.35) and the nmr (δ 1.60, 2.23 (t), and 3.17 with relative areas 1:17.5:7.5) showed that a drastic change in the structure took place.

Oxidation of 4 in Aqueous Acetic Acid. The procedure was identical with that in anhydrous acetic acid. Cinnamyl alcohol was identified by its retention time on the XF-1150 column (31 min, at 155°, 15 psi of He).

Reaction of 4 with Acid. 4 (1.41 g) was added to HClO₄ (42 mM) in AcOH (50 ml), and the mixture was kept for 35 hr at 75°. After the usual work-up seven compounds including 4 were formed. The main product (by ir and retention time) is 2-acetoxy-1-phenylpropane. Some **3** was also formed.

Reaction of 3 with Perchloric Acid. To 3 (4.87 g) in AcOH (20 ml), HClO₄ (0.52 M) in AcOH (4 ml) was added. Heat was evolved and the solution turned yellow immediately, then red, and it darkened rapidly. After 1 hr the mixture was poured into water, extracted with methylene chloride (70 ml), washed (aqueous NaHCO₃), and dried (Na₂SO₄), and the solvent was evaporated. 3 was extracted (pentane) leaving a viscous oil which could not be induced to crystallize (aqueous acetone, methylene chloride-pentane) with ir similar to that of 3.

Oxidation of the C_nH_{2n} Olefins. A 1:1 mixture of 1-olefin and Hg(OAc)₂ or a 1:1 or a 1:2 mixture of 2-olefin with Hg(OAc)₂ in acetic acid was kept at 75° for 7-10 days, or at reflux for several hours. Hg was formed from the 1-olefins and Hg₂(OAc)₂ from the 2-olefins. The mixture was poured into saturated K₂CO₃ solution, extracted with pentane, and dried (Na₂SO₄), the solvent was evaporated and the esters (which were in a ratio close to the equilibrium value) were separated and analyzed on an XF-1150 column. The best separation conditions are given in Table VIII. The analyses, nmr, and ir of the allylic esters are given in Table IX. In the oxidation of 1-phenyl-3-pentene (8.9 g) by Hg(OAc)₂ (18.2 g) in AcOH (35 ml) at 75° for 20 days two nonolefinic compounds were collected, but only the one with the longer retention time was isolated and identified as 1-acetoxy-5-phenyl-2-pentene.

Olefins from the Oxidation of the Butenes. The reaction mixture from the oxidation of 1-butene (2.2 M) with Hg(OAc)₂ (1.57 M) in AcOH at 75° for 17 days was poured into cold K₂CO₃ solution, extracted with toluene, and analyzed on a 3-m saturated AgNO₃-ethylene glycol on Firebrick column. At 37°, a He pressure of 8 psi, peaks at 2.5 (11), 8.5 (10), 9.3 (9), and 46 min (toluene) were observed.

Similar analysis from the oxidation mixture of cis-2-butene (0.57 M) with Hg(OAc)₂ (0.11 M) for 94 hr at 75° gave a cis-2-butene-trans-2-butene ratio of ca. 0.33. Traces of 1-butene were also formed, but the peak is mainly covered by the cis-2-butene peak.

Kinetic Procedure. (a) By Vpc. Except for the gaseous olefins, stock solutions of the two reactants in acetic acid were prepared. Those of the olefins were stable for months, while those of Hg(OAc)₂ gave some Hg₂(OAc)₂ after 1 month, and were used within a few days of their preparation. The reagents and the vpc standard were mixed at room temperature and kept at 75°. Samples were withdrawn, poured into saturated K₂CO₃ solution, and extracted twice with pentane (50 ml), the extract was washed with saturated K₂CO₃ solution (100 ml) and dried (Na₂SO₄), the solvent was evaporated at 40-60° in vacuo, and the residue was analyzed by vpc.[48] The gaseous olefins were absorbed by a suspension of Hg(OAc)₂ and their concentrations were determined from the change in weight.

(b) By Gravimetry. The reaction was conducted in 25-ml flasks. At predetermined times the contents of the flask were shaken until the mercury formed one droplet. The solution was transferred at the reaction temperature to another 25-ml flask without the Hg droplet. Losses due to transfer were small and were taken into account. The droplet was washed, dried, and weighed. When Hg₂(OAc)₂ was also formed it was separated easily from the droplet, filtered, and dried, and its amount (as Hg) was added to that of the metallic Hg.

The kinetics of the solvolysis of 1 was followed by vpc. A sample run is given in Table X.

Warning. In preparative vpc of the oxidation mixture some of the organomercury adducts are partially extracted into the ether, and decompose on the vpc column, liberating metallic mercury.

(48) The extraction was found to be complete under these conditions. The response of the allylic acetates to the vpc detector was calibrated.

Metal Acetate Promoted Reactions of σ and πAllylic Organometallics

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Abstract: The reactions of the allylic mercurials, trans RCH=CHCH₂HgOCOCH₃ (R = CH₃ or C₆H₅), either alone or with added metal acetates, M(OAc)$_n$, where M = Hg (n = 2), Pb (n = 4), Tl (n = 3), and Pd (n = 2), in acetic acid have been investigated. Product distributions, either extrapolated to zero time or based on very early observations, have been measured and in the cases of Pb(IV) and Tl(III) the production of substantial amounts of cis-crotyl acetate is interpreted in terms of SEi' formation of allylic derivatives of these metals, which then demetalate. The dimeric π-crotyl- and π-cinnamylpalladium acetates have also been examined alone, or in the presence of M(OAc)$_n$ as outlined above, in acetic acid and DMSO-acetic acid (9:1). Neutral depalladation, i.e., in acetic acid, is suggested to involve rate-determining formation of a σ-allyl species which may then undergo rapidly a number of product-determining depalladations. Reactions with Tl(OAc)₃ may involve formation of a σ-allyl species (to account for cis product from trans-crotylpalladium complex) as well as direct oxidation of the π complex. This latter path seems quite likely for Pb(OAc)₄ where the crotyl acetate product is completely trans, although the same stereochemical result would be anticipated for the intervention of a crotyl cation.

There are conceptually a number of ways by which allylic oxidation of an olefin by M(OAc)$_n$ (M = Hg(II), Pd(II), Tl(III), Pb(IV)) can occur. A particularly attractive pathway involves the formation and sub-

sequent demetallation of an allylic organometallic, and this sequence has been suggested for the Hg(OAc)₂ oxidation of certain olefins in acetic acid.[2a] In contrast, under some conditions, the most plausible mechanism for Pd(OAc)₂ oxidation of the butenes does not seem to

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