Reaction of 3 with Perchloric Acid. To **3** (4.87 g) in AcOH (20 ml), $HClO_4$ (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 $NaHCO_3$), and dried (Na_2SO_4), 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 $Hg_2(OAc)_2$ from the 2-olefins. The mixture was poured into saturated K_2CO_3 solution, extracted with pentane, and dried (Na_2SO_4), 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 K_2CO_3 solution, extracted with toluene, and analyzed on a 3-m saturated $AgNO_3$–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 $Hg_2(OAc)_2$ 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 K_2CO_3 solution, and extracted twice with pentane (50 ml), the extract was washed with saturated K_2CO_3 solution (100 ml) and dried (Na_2SO_4), 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 $Hg_2(OAc)_2$ 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.

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[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 π Allylic Organometallics

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Abstract: The reactions of the allylic mercurials, trans $RCH{=}CHCH_2HgOCOCH_3$ ($R = CH_3$ or C_6H_5), 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 subsequent 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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[2] (a) Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, 5119 (1965); (b) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966).

Table I. Reactions of $RCH{=}CHCH_2HgOAc$ with Equimolar Metal Acetates in Acetic Acid

System	R =	Added salt	k_1, sec^{-1}	$RCH{=}CHCH_2OAc$(P) Cis	Trans	RC(OAc)-HCH=CH$_2$ (S)	Yield (%) of allylic acetates	Inorganic product
1	CH_3	None^a	8×10^{-7}			99.5	84	Hg (0)
2	CH_3	$Hg(OAc)_2$^{a}	2.2×10^{-4}			99.5	90	Hg(I)
3	CH_3	$Tl(OAc)_3$^{a}	*Ca.* 5.5×10^{-2} ^{d}	14.0	32.0	54.2	75	Tl(I); Hg(II)
4	CH_3	$Pb(OAc)_4$^{a}	Very fast^e	50.6	4.4	45	92	Pb(II); Hg(II)
5	CH_3	$Pd(OAc)_2$^{a}	*Ca.* 8×10^{-6}	2	8	90	*f*	Pd(0); Hg(II)
6	C_6H_5	None^b	6×10^{-4}	60		40	95	Hg(0)
7	C_6H_5	$Hg(OAc)_2$^{b}	*f*	60		40	95	Hg(I)
8	C_6H_5	$Tl(OAc)_3$^{c}	Very fast^e	43		57	95	Tl(I); Hg(II)
9	C_6H_5	$Pb(OAc)_4$^{c}	Very fast^e	19		81	90	Pb(II); Hg(II)

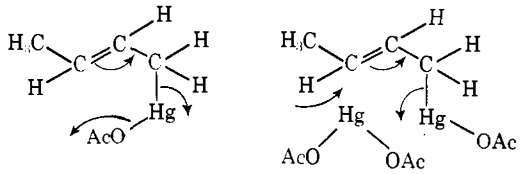
[a] At 25°. [b] At 75°. [c] At 50°. [d] From a one-point determination and very approximate. [e] The *ca.* 90% yields of allylic acetates obtained in less than 2 min, and in some cases in 30 sec. [f] Not determined.

involve a π-allylpalladium species as a key intermediate.[2b] Since σ-allyl derivatives of mercury and π-allyl derivatives of palladium can be synthesized and their solvolytic demetallation studied, experimental tests for their intervention in allylic oxidation are essentially straightforward. In other cases, however, such as allylic oxidation by $Pb(OAc)_4$ and $Tl(OAc)_3$, the situation is more difficult since synthesis and isolation of $RPb(OAc)_3$ and $RTl(OAc)_2$ (R = allylic group) is not easy (due to facile demetallation) and in fact has not been accomplished.[3,4] An appealing method for at least *in situ* generation of such allylic lead and thallium compounds involves allylic ligand transfer from either mercury or palladium, and our initial experiments revealed results of such interest that extension beyond the area of relevance to olefin oxidation was deemed necessary. In this paper we describe the reactions of certain σ-allylmercurials and π-allylpalladium compounds with electrophilic metal salts ($M(OAc)_n$ where M = Hg(II), Pb(IV), Tl(III), . . .) and outline possible mechanisms.

Results and Discussion

The presentation falls logically into two parts and firstly we discuss the reactions of certain σ-allylmercuric acetates with $M(OAc)_n$, and follow this with the reactions of the π-bonded allylpalladium systems.

(a) Reactions of Allylic Mercuric Acetates. A previous report described the neutral and $Hg(OAc)_2$-promoted demercurations of crotylmercuric acetate,[2a] both of which led to rearranged acetate almost exclusively, and the mechanisms below were suggested.



The high reactivity of allylic mercurials generally and the report by Criegee[5] that dialkylmercurials reacted with $Pb(OAc)_4$ prompted us to extend the study to include $Pb(OAc)_4$, $Tl(OAc)_3$, and $Pd(OAc)_2$ as promoters. Both crotyl- and, to a lesser extent, cinnamylmercuric acetate have been examined in this way, and the details are located in Table I.

The rate constants quoted are calculated on the basis of first-order disappearance of mercurial, and zero-order disappearance in added salt, and their chief significance is to focus on the very different disappearance rates of mercurial in the presence of $M(OAc)_n$.

The product distributions refer to very early determinations or are extrapolated from distribution–time curves. These procedures, to ensure distributions related to kinetic control, are necessary since $Hg(OAc)_2$ (either added or a reaction product) and $Pd(OAc)_2$ are efficient primary–secondary and cis–trans isomerization catalysts.[6] The order of efficiency of $M(OAc)_n$ as isomerization catalysts is $Pd(OAc)_2 > Hg(OAc)_2 \gg Pb(OAc)_4$ or $Tl(OAc)_3$.

Systems 1 and 2 have been discussed in another connection,[2a] but on comparison with systems 3 and 4 it is clear that $Tl(OAc)_3$ and $Pb(OAc)_4$ react quite rapidly with crotylmercuric acetate to produce a very altered product pattern among the allylic acetates, which are formed in high yield. The type of mechanisms suggested for $Hg(OAc)_2$ "promotion" is clearly largely supplanted in systems 3 and 4. The starting crotylmercuric acetate has been shown to be σ and trans[7-9] and hence it appears that any *cis*-crotyl acetate produced (under conditions of kinetic control) must involve at some stage the intervention of a covalent α-methallyl derivative. Thus, the products may arise from SN1 or SNi′ demetallation of transiently formed allylic lead or thallium derivatives, and the product distribution may reflect differing degrees of SE2 (or SEi) and SE2′ (or SEi′) formation of these intermediates, as depicted below for the $Pb(OAc)_4$ case and which may be generalized.

The intermediate butenyllead (or -thallium) intermediate may simply demetalate (SN1) and in these cases the leaving groups would be somewhat complex and could influence subsequent solvent attack on the carbonium ion. For butenyl metal systems (including mercury)[2a,7,9] that have been studied,[1c-12] the primary–

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(3) See, however, T. Abe, H. Kurosawa, and R. Okawara, *J. Organometal. Chem.*, **25**, 353 (1970).

(4) W. Kitching, *Organometal. Chem. Rev.*, **3**, 5 (1968).

(5) R. Criegee, P. Dimroth, and R. Schempt, *Chem. Ber.*, **90**, 1337 (1957).

(6) Unpublished results.

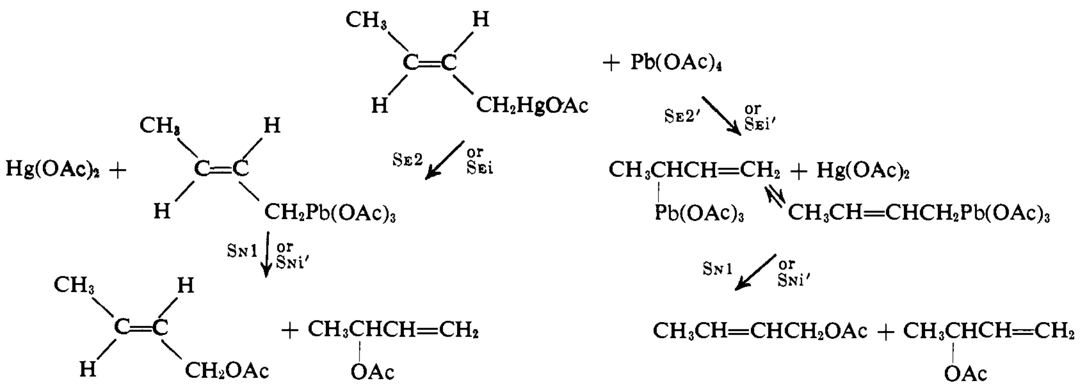
(7) P. D. Sleezer, Ph.D. Dissertation, University of California at Los Angeles, 1963.

(8) P. D. Sleezer, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **85**, 1890 (1963).

(9) W. Kitching, P. D. Sleezer, M. Bullpitt, S. Winstein, and W. G. Young, *J. Organometal. Chem.*, **34**, 321 (1972).

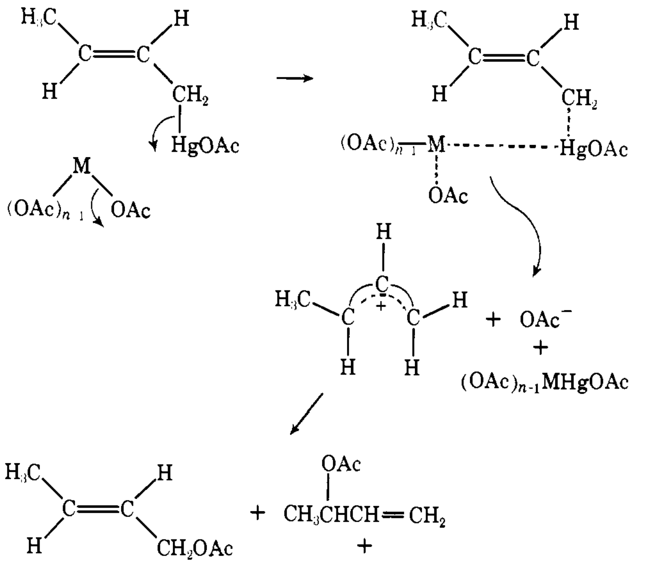
(10) J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 494 (1961).

(11) C. W. Fong and W. Kitching, *Aust. J. Chem.*, **22**, 471 (1969).



secondary equilibrium is heavily in favor of the former, and there seems no good reason to suppose a difference for isoelectronic lead or thallium cases. Nevertheless, demetalation from the secondary α-methallyl metallic may be significant, without being substantial. This matter, however, is really a question of relative rates of allylic metallic equilibration and demetalation, on which we have no information, except that the latter and probably the former is relatively fast.

Another component of the mechanistic picture may not involve formation of carbon–lead or carbon–thallium bonds, but that the added salt attacks on mercury and accelerates carbon–mercury bond cleavage in this way.[13–15]



Although the formation of a Hg–Hg bond in the $Hg(OAc)_2$ promotion has been suggested, it is unclear that Hg–Tl or Hg–Pb bonds will be formed with equal facility. In any case, the substantial amounts of *cis*-crotyl acetate produced in systems 3 and 4 indicate that the above scheme cannot be operative solely (butenyl carbonium ions preserve configuration)[8,16] and it may well be minor.

There are good grounds for supposing that with $Pb(OAc)_4$ and $Tl(OAc)_3$ the major pathway is the SE′ (probably SEi′) formation[1,8] of butenyl metallics which demetalate. The enhanced reaction rates, production of *cis*-crotyl acetate, and the two-electron reduction suffered by the "promoter" are in harmony with this scheme. Although there may be an SE2 component, this could well be minor, as in protic acid cleavage (*e.g.*, HCl) of crotyl mercurials[8] SE2 (or SEi) competes indetectably with SE′ (probably SEi′). Admittedly, the steric features of the $M(OAc)_n$ reactions may be more demanding than those in acid cleavage, perhaps leading to some SE2 or SEi component.

Probably the most striking feature of the results is the very high content of *cis*-crotyl acetate in system 4, which seems to imply interesting conformational preferences in the intermediate organometallic. If in the α-methallyllead triacetate, that conformation placing β-hydrogens cis to the double bond, and allowing carbon–metal (σ–π) hyperconjugation is favored, a *cis*-crotyl cation could be formed preferentially.[17] The $Pb(OAc)_4$ and $Tl(OAc)_3$ reactions produce more crotyl acetate than perchloric acid catalyzed demercuration (71% secondary:29% primary)[8] where the double bond is considered to participate greatly in the bond breaking step, and where specific solvation appears to be minimal.[18] It would be of considerable importance to study the behavior of both α-methallylmercuric and *cis*-crotylmercuric compounds, but synthetic problems here are quite formidable.

The $Pd(OAc)_2$ reaction (systems), resulting in a high proportion of secondary acetate, suggests a mechanism of the type below.

The discrete formation of a Pd–Hg bonded species, *e.g.*, $(AcOPd\text{-}HgOAc)_x$, may be involved, rather than a more synchronous scheme as portrayed. This mechanism is in line with the qualitative impression that $Pd(OAc)_2$ is not a strong electrophile.

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[12] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

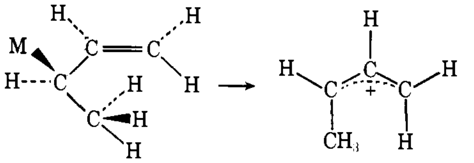
[13] E. Vogelfanger, Dissertation, University of California, Los Angeles, 1963.

[14] K. Ichikawa and H. Ouchi, *J. Amer. Chem. Soc.*, **82**, 3876 (1960).

[15] G. F. Wright and J. H. Robson, *Can. J. Chem.*, **38**, 1, 21 (1960).

[16] W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960).

[17] Two factors may operate to make the conformation below most favored for α-methallyllead triacetate: (a) the operation of σ–π (carbon–metal) conjugation (*e.g.*, see W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970)) and (b) a presumed favored conformation for 1-butenyl compounds, which places β-hydrogens cis to the double bond (see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 196). The reasons for the substantial difference between the



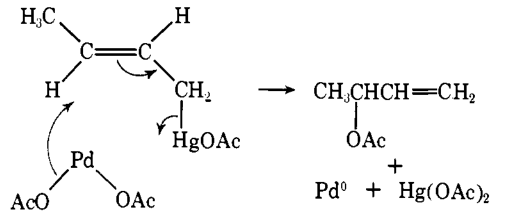
cis components for $Pb(OAc)_4$ and $Tl(OAc)_3$ reactions are not completely clear.

[18] See F. R. Jenzen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4477 (1961), and subsequent papers.

Table II

System	Complex	Solvent	Promoter	10^5k_1, sec^{-1}	Yield (%) of allylic acetates	Product distribution: *sec*-OAc	Cis primary OAc	Trans primary OAc	Cinnamyl CHO	Other
10	I[a]	AcOH		1.8 ± 0.4	21	91	0.9	8.1		
11	I[a]	DMSO-AcOH		9.5 ± 0.5	30	47.0	7.1	45.9		
12	I	AcOH	$Tl(OAc)_3$	3.9 ± 0.3	64	79.2	1.3	19.5		
13	I	DMSO-AcOH	$Tl(OAc)_3$	24 ± 6	54	77.2	1.1	21.7		
14	I	AcOH	$Pb(OAc)_4$	290 ± 80	75	80.8		19.2 (t = 99.5)		
15	I	DMSO-AcOH	$Pb(OAc)_4$	*Ca.* 100	50	70.4		19.6 (t = 98)		
16	II[a]	AcOH		6.9 ± 0.1		10		32	57.5	0.5[c]
17	II[a]	DMSO-AcOH		61 ± 1	84			96		4[c]
18	II[b]	AcOH	$Tl(OAc)_3$	17 ± 3	55	70.0		30		
19	II[b]	DMSO-AcOH	$Tl(OAc)_3$	73 ± 8	40	0.6		99.4		
20	II[b]	AcOH	$Pb(OAc)_4$	*Ca.* 600	67	69.4		26		
21	II[b]	DMSO-AcOH	$Pb(OAc)_4$	*Ca.* 400		0.5		86	11.5	2.0

[a] At 75°. Other results pertain to room temperature. [b] Cis component not determined. [c] From vpc behavior it appeared to be β-methylstyrene.



$$\longrightarrow \underset{\text{OAc}}{CH_3CHCH{=}CH_2} + Pd^0 + Hg(OAc)_2$$

The mechanism most appropriate for neutral demercuration of cinnamylmercuric acetate (system 6), in which comparable amounts of both allylic isomers are formed, would seem to require a carbonium ion description,[7,19] rather than SNi′, suggested[2a] for the crotylmercuric acetate (system 6). $Hg(OAc)_2$ acceleration (system 7) probably originates from attack at the mercury atom.

$Tl(OAc)_3$ and $Pb(OAc)_4$ react (systems 8 and 9) very rapidly with cinnamylmercuric acetate to produce the cinnamyl acetate and α-phenylallyl acetate in high yield. The isomer distributions in the product differ substantially in the two cases, and would seem to reflect a difference in the degrees of SE and SE′ attack and also possible differences in the natures of the carbonium ions formed in deplumbation and dethallation. The relative extent of $M(OAc)_x$ assistance to ionization of the cinnamyl–mercury bond may also vary. It is of interest to point out that these distributions (8 and 9) are substantially different from that in the AgOAc-catalyzed solvolysis of cinnamyl chloride in acetic acid,[20] where 37% α-phenylallyl acetate was obtained. This latter figure is, however, similar to that found in neutral demercuration of cinnamylmercuric acetate. Determination of the cis content in the cinnamyl acetate was unfortunately not possible.

The sequence (below) suggested by Criegee[5] to explain his data for the $R_2Hg + Pb(OAc)_4$ reactions is strong support for the above proposals in which intermediate allylic lead and thallium compounds are involved.

$$R_2Hg + Pb(OAc)_4 \longrightarrow RPb(OAc)_3 + RHgOAc\ (S_E)\ (R = \text{alkyl})$$

$$RPb(OAc)_3 \longrightarrow R^+ + Pb(OAc)_2 + OAc^-\ (S_N1)$$

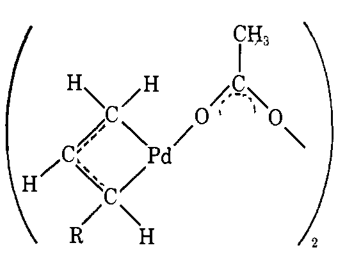
$$R^+ \longrightarrow ROAc + \text{olefin}$$

Strong evidence for carbonium ion involvement followed from rearranged products in the case of neopentyl. Since allylic mercurials are enormously more susceptible to electrophilic attack than saturated organomercurials,[8] rapid SE formation (probably largely SE′) of allylic lead or thallium compounds appears difficult to resist. For steric and electronic reasons, SE′ may be less favored with cinnamylmercury systems (8 and 9).

(b) Allylic Palladium Systems. Having examined the σ-allylmercury systems, it appeared desirable to provide comparative data for the related π-allylpalladium acetate systems, since here, depending on conditions, reaction *via* the π or σ form was possible. In addition, recent discussions on Pd(II) oxidations of simple olefins, which have been suggested under certain circumstances to involve π-allylpalladium intermediates,[21] render it essential to provide data on depalladation reactions of simple allylic palladium compounds.

The compounds chosen for study were the dimeric π-crotyl- and π-cinnamylpalladium acetates,[22] and these complexes were solvolyzed in acetic acid and in dimethyl sulfoxide–acetic acid (9:1 by weight) either alone or with $Tl(OAc)_3$ and $Pb(OAc)_4$ as promoters.

$(\pi\text{-crotyl PdOAc})_2$



I, $R = CH_3$
II, $R = C_6H_5$

Neutral Solvolysis at 75°. The results are shown in Table II, and product distributions are extrapolated values at zero time.

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[19] Z. Rappoport, L. K. Dyall, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, 3483 (1970).

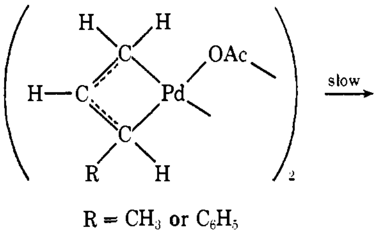
[20] See R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[21] See for example, R. G. Brown, J. M. Davidson, and C. Triggs, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, p 23B.

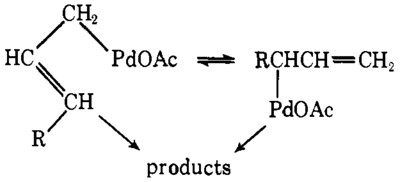
[22] (a) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964); (b) S. D. Robinson and B. L. Shaw, *J. Organometal. Chem.*, 3, 367 (1965).

Since DMSO causes an acceleration in solvolysis of the complexes, a plausible scheme would involve the intermediacy of a σ-allylpalladium complex, formed in the rate-determining step, followed by reaction to yield the products. Although olefin formation can be substantial, as it is in neutral solvolysis of allylmercuric acetate, the details of its formation are unclear.[23]

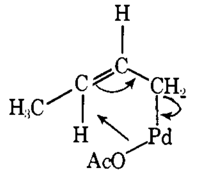
Thus for I and II we can write



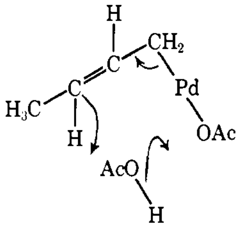
R = CH_3 or C_6H_5



with the equilibrium between the σ species being heavily in favor of the primary form. For complex I, which yields 90% secondary acetate, SNi′ depalladation is likely, although a mechanism (we label SNs′ (see below)) plausible because of palladium's affinity for hydride requires serious consideration.



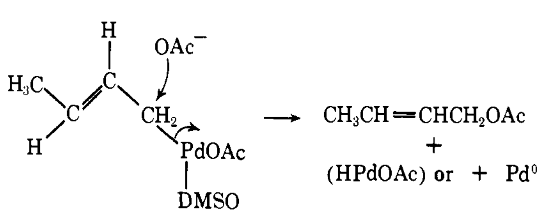
SNi



SNs

Such mechanisms when applied to the secondary σ-allylpalladium species would yield primary acetate which is a minor product.[24]

Besides causing significant rate accelerations for I, DMSO is responsible for different product distributions, mainly in the direction of the increased component of primary acetate. We view this as being evidence for the incursion of another mechanism—SN2 displacement by acetate at the primary carbon. This route may apply to I in DMSO–AcOH so that we have rate-determining formation of a σ complex, but product-determining decomposition of it, dependent on solvent. In DMSO–AcOH mixtures, the concentration and effectiveness of acetate may be increased. Since the primary σ-allyl form is favored, this SN2 displacement will yield primary acetate as shown.



The solvolysis of the cinnamyl systems presents a quite different picture in that substantial amounts of cinnamaldehyde were produced, while the secondary acetate component is quite small. Isomerization of α-phenylallyl acetate in the presence of $Pd(OAc)_2$ in AcOH yields cinnamyl acetate, but no cinnamaldehyde was produced, indicating the latter to be formed in the solvolysis in a "primary" process. Since the "zero-time" extrapolated products are predominantly primary, it is important to check the isomerization rates of α-methallyl acetate, which is found in the π-crotyl Pd solvolysis in predominant amount. The comparison is made below in Table III, showing the ratio of pseudo-first-order solvolysis constants of each of I and II to the isomerization rate constant of the corresponding secondary acetate, at 75°.

Table III. k_1 (solvolysis)/K_1 (isomerization)

Complex	AcOH	DMSO–AcOH
I	*Ca.* 0.2	*Ca.* 6
II	*Ca.* 1	*Ca.* 5.5

Thus, isomerization is not important in the solvolysis of II and I. This seems to suggest that the SN2 route, yielding primary product from the primary σ-cinnamylpalladium complex, is predominating with SNi′ and SNs′ relatively unimportant. This proposal is reasonable on the grounds that SNi′ and SNs′ remove the double bond from phenyl conjugation which is a far more serious impediment than methyl (hyper) conjugation for the crotyl systems. The more severe steric features of the phenyl group may also be important, hindering the formation of secondary product. Formation of aldehyde then appears to be due to involvement of H_2O, present in concentrations (Karl–Fischer titration) comparable with the starting cinnamyl complexes. Huttel[25] has demonstrated that π-allylpalladium complexes in the presence of $PdCl_2$ in AcOH–H_2O yield unsaturated aldehydes or ketones, and a mechanism along similar lines, perhaps involving also the σ-cinnamyl species, could explain the formation of cinnamaldehyde. The yield of cinnamaldehyde increased when *ca.* 5% aqueous acetic acid was empolyed as solvent.

A remarkable result is the almost complete suppression of aldehyde in the presence of DMSO–AcOH, where 96% of product is *trans*-cinnamyl acetate, and SN2 displacement by OAc^- is favored.

$M(OAc)_n$-Promoted Solvolyses of Allylpalladium Compounds. The results obtained for $Tl(OAc)_3$ reactions of the complexes are listed in Table II. These pertain to room temperature and for equimolar concentrations.

In comparing the data in Table II, it is seen that the presence of $Tl(OAc)_3$ results in modest rate enhancements and altered product distributions. The rate increases cannot be explained by a $\pi \rightarrow \sigma$ conversion as the sole rate step (prior to rapid interception by Tl-

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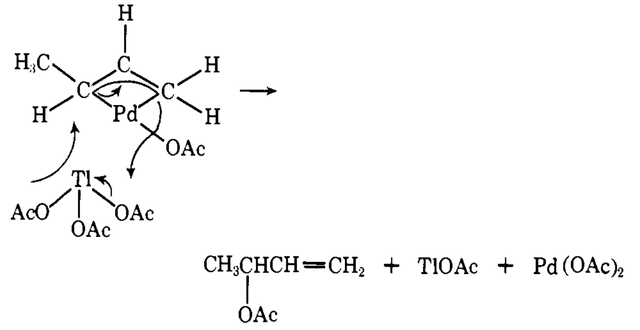
[23] In the neutral solvolysis of I, the butene mixture found had the following composition: 1-butene, 10%; *cis*-2-butene, 57%; *trans*-2-butene, 33%.

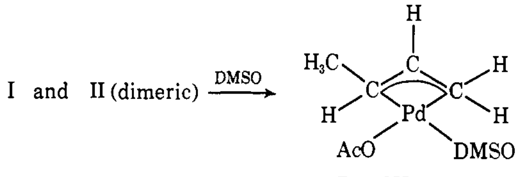
[24] The results in systems 5 and 10 are quite similar, but the kinetics argue against prior formation of crotylpalladium acetate in 5.

[25] R. Hüttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961); R. Hüttel and H. Christ, *ibid.*, **97**, 1439 (1964).

(OAc)$_3$ or some derived species); otherwise the rate constant for the neutral depalladation, after allowing for temperature difference, would agree with the appropriate constant above. Rather, at least two mechanisms seem operative. Tl(OAc)$_3$ attack on the σ complex (as already discussed for the σ-allyl mercurials) (which could account for the cis product) may be of comparable importance with direct attack on the π complex, during which loss of configuration may not be possible. The high trans content in both entries for the crotyl system would favor this latter route, as drawn below, while similar attack could occur at the primary carbon to yield *trans*-crotyl acetate. By making reasonable rate extrapolation to 75°, and comparing with the neutral solvolysis data, Tl(OAc)$_3$ for I results in a rate enhancement of *ca.* 60–70 and thus attack on the π complex may be the most important component.



DMSO has quite pronounced but variable effects on rates and products. Thus, it accelerates the reactions of I and II, and in the latter case changes the product from 70% secondary acetate to almost pure primary acetate. DMSO could promote the breakdown of the dimeric structure of Ia and IIa to the type of "asymmetric" π complex shown below.

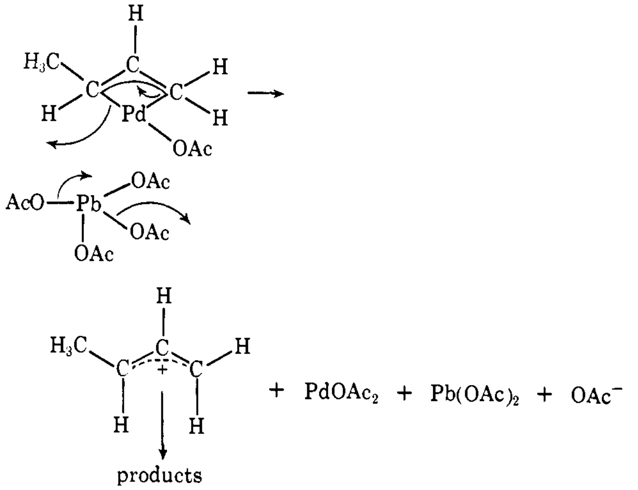


R = CH$_3$, C$_6$H$_5$

This new species in the case of I could be more susceptible to TlOAc$_3$ attack, without drastically altering the product distribution. However, in the case of II a dramatic product change indicates almost exclusive attack at the primary carbon. Steric effects, since TlOAc$_3$ probably exists as Tl(OAc)$_3$(DMSO)$_x$, may be quite serious in the region of the secondary carbon.

Solvolysis Promoted by Equimolar Pb(OAc)$_4$. The results are assembled in Table II. Pb(OAc)$_4$ reactions are very fast and DMSO in part decreases the rates for both complexes. This rate reduction may be due to complexation and its steric consequences. The remarkable specificities for I (almost exclusively trans and trans starting complex) argue strongly against the intervention of a σ-allyl species.

For I, the product distribution is remarkably similar to that found in HClO$_4$-catalyzed demercuration (71% secondary:29% primary, $t > 99.5$)[8] so that a carbonium ion description merits consideration (for Tl(OAc)$_3$ as well) and could be formed as below. The crotyl cation is known to preserve its configuration.[8,16]



On the other hand, crotyl ligand transfer to lead to form crotyllead triacetate (which demetalates) is plausible, but the absence of cis product is troublesome for this suggestion. It is of importance that Hg(OAc)$_2$ also reacts readily with I in AcOH to yield 25.6% primary OAc (>99% trans) and 74.4% secondary OAc (yield ~ 70%), very similar to the Pb(OAc)$_4$ results. Since crotylmercuric acetate would be stable under these conditions[2a] (and in any case yields almost exclusively secondary acetate on neutral and Hg(OAc)$_2$-promoted demercuration) it seems unlikely that crotyl ligand transfer to lead is important. Direct attack on the π complex as already drawn for Tl(OAc)$_3$, which would preserve the *trans*-crotyl structure, appears most likely for I.

The situation for II is not straightforward, and although the cinnamyl acetate appeared to be exclusively trans, at equilibrium trans heavily predominates in cinnamyl acetate. If the trans product is due to kinetic control, a mechanism of direct oxidation of the π complexes would again be valid. Extensions to other σ- and π-allyl metallics would be most fruitful and is currently being undertaken.

Experimental Section

Synthesis of Allylic Metallics. Mercurials. The allylmercury compounds had analyses and pmr and ir spectra in accordance with the assigned structures, and their preparation and properties will be described elsewhere.[9]

Palladium Compounds. The complexes were synthesized essentially by the method of Dent, Long, and Wilkinson.[22a] Silver acetate in acetone converted the chloro to the acetato complexes.[22b]

The compounds have the trans configurations on the basis of pmr studies.

π-Crotylpalladium chloride showed bp 137–140° dec (lit.[22a] 136–137°).

π-Cinnamylpalladium chloride showed bp 198–203° dec (lit.[22a] 195–200°).

π-Crotylpalladium acetate[22b] showed bp 108–117° dec. The ir spectrum (10% CHCl$_3$ solution) shows very strong peaks at 1570 and 1420 cm^{-1} (bridged acetate group).

Anal. Calcd for C$_6$H$_{10}$O$_2$Pd: C, 32.66; H, 4.53. Found: C, 33.08; H, 4.67.

π-Cinnamylpalladium acetate showed bp 169–177° dec; ir shows bridged acetate peaks at 1560 and 1420 cm^{-1}.

Anal. Calcd for C$_{22}$H$_{24}$O$_4$Pd$_2$: C, 46.74; H, 4.38. Found: C, 46.80; H, 4.46.

Acetic acid of >99% purity was refluxed overnight with acetic anhydride (*ca.* 40 g/3 l. of acid) and then distilled under dry N$_2$ gas.

Mercuric acetate, lead tetraacetate, and palladium acetate (Engelhard Industries) were commercially available. Thallic acetate was prepared from Tl$_2$O$_3$ and acetic acid.

Table IV

Compd	Retention time, min	Factor[a] (f)
n-Butyl OAc	16.1–16.5	1.00 (defined)
α-Methallyl OAc	10.4–10.8	1.00
cis-Crotyl OAc	21.0–21.3	0.888
trans-Crotyl OAc	22.5–22.8	0.968

[a] Factor was defined as $W_1/W_0 = f_1A_1/f_0A_0$, where W_1 = weight of compound 1; A_1 = area of compound 1; W_0 = weight of standard *n*-BuOAc; A_0 = area of standard; f_0 defined is 1.00.

***n*-Butyl Acetate.** Eastman Kodak white label material was redistilled, bp 125°, and showed a single peak on vpc analysis.

α-Methallyl acetate was prepared as described by Prevost[26] from α-methallyl alcohol and acetic anhydride, bp 111° (lit. 112°). The material was homogeneous on vpc analysis and the ir and nmr data were in accord with the secondary structure.

Crotyl acetate was prepared as described by Charon[27] from crotyl alcohol and acetic anhydride; bp 131° (lit. 128–129°). The product had nmr and ir spectra in accord with the primary structure, and cis and trans isomers were separable on a 4.8% tricresyl phosphate on Chromosorb W (80–100) column.

Alternatively, *cis*-crotyl acetate was prepared from *cis*-crotyl alcohol and acetic anhydride in pyridine. *cis*-Crotyl acetate was separated by distillation and was pure on vpc analysis.

α-Phenylallyl acetate prepared from the esterification of the alcohol (from acrolein and phenylmagnesium bromide, bp 81–85° (2 mm); $n^{25}\text{D}$ 1.5355) with acetic anhydride had bp 92° (2 mm); $n^{22}\text{D}$ 1.5085.

Cinnamyl acetate was prepared by esterifying cinnamyl alcohol with acetic anhydride: bp 113° (2.4 mm); $n^{29}\text{D}$ 1.543. It was 99% pure by vpc analysis.

Cinnamaldehyde was commercially available.

Calibration of Vapor Phase Chromatography. The amounts of solvolytic products were calculated from the area of each integrated vpc peak relative to that of a standard. A linear relation between area ratio and weight ratio was demonstrated and calibration factors of each compound were calculated.

Butenyl Acetates. Vpc was performed on a Perkin-Elmer 800 analytical gas chromatograph on a tricresyl phosphate 4.8% on Chromosorb W 80–100, 20-ft column, wih a column temperature of 70° and an injector temperature of 120°, with the carrier gas N_2 (355.5 psi) (see Table IV).

Phenylallylic Acetates. The calibration method was similar except for the different vpc conditions: XF-1150 10% on Chromosorb W (80–100) 2-m column; column temperature, 150°; injector temperature, 170°; carrier gas N_2 (35 psi) (see Table V). Under the above conditions the following retention times were found for minor products (f values not determined): allylbenzene, 2.0 min; α-methylstyrene, 2.3 min; β-methylstyrene, cis 2.8 min, trans 5.0 min.

Solvolysis. Experimental Procedure. The procedures employed for the mercurials and the palladium compounds are essentially the same and the following serves to illustrate the method.

Table V

Compound	Retention time, min	Factor (f)
Diethyl adipate	16.4–16.8	1.00 (defined)
α-Phenylallyl OAc	9.3–9.5	0.729
cis-Cinnamyl OAc	18.1–18.6	0.764
trans-Cinnamyl OAc	30.5–31.0	0.730
trans-Cinnamaldehyde	27.6–27.9	1.00

A small glass container, fitted with a rubber serum cap, which contained *ca.* 0.1 mol (8.12 mg) of the precisely weighed standard compound and 2.5 ml of solvent and, if necessary, a known equimolar (or other) weight of promoting salt ($(M(OAc))_n$), was maintained at 75°, 50°, or room temperature. During the reaction 0.5 ml of sample was taken by means of a syringe and poured slowly into 2.5 ml of saturated K_2CO_3 aqueous solution at 0°. After 3 ml of distilled water was added to this mixture, it was extracted by 2.5 ml of cold pentane. This pentane layer was separated and dried with anhydrous $CaCl_2$.

Analysis of the pentane solution was then conducted by vpc under the same conditions used in calibration.

Identification of Solvolytic Products. α-Methallyl acetate and *cis*- and *trans*-crotyl acetates from the solvolysis of the butenyl metallics were separated and identified by, in most cases, all, or a combination, of vpc characteristics on more than one column under different conditions, elemental analyses, and ir and nmr comparisons with authentic specimens. Similarly, α-phenylallyl acetate and cinnamyl acetate were identified.

The compound obtained in neutral solvolysis of π-cinnamyl $PdOAc_2$ showed a vpc peak at exactly the same retention time as that of *trans*-cinnamaldehyde, but could not be separated from *trans*-cinnamyl acetate by attempted preparative vpc. The mixture gave a red precipitate with 2,4-dinitrophenylhydrazine and a positive Tollens test, not yielded by cinnamyl acetate alone. The percentage of this compound increased significantly when 5% aqueous acetic acid was employed as solvent instead of the refined acid.

Rate constants at the initial step of solvolysis were calculated from time-yield relationships and were expressed by the average of two or three points and range (R). k_1 = average ± $R/2$. Here, $R = (k_1)_{\max} - (k_1)_{\min}$.

Although olefin production is substantial in some cases, the rate constants, being based on rate of production of acetate products, refer to the kinetics of disappearance of starting compound by these routes.

In the cases of the promoted reactions of the mercurials, treatment of the data as second-order overall, *i.e.*, first order in mercurial and first order in added salt, gave steadily increasing rate constants, and the rate constants reported in the text were obtained by treating the reactions as first order in mercurial and zero order in added salt.

The rates of isomerization of secondary allylic acetates reported here were calculated by the procedures outlined for treatment of the solvolysis data. Further details of data treatment are in the M.Sc. Thesis of T. Sakakiyama, University of California at Los Angeles, 1969.

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(26) C. Prevost, *Ann. Chim.* (*Paris*), [10] **10**, 147 (1928).

(27) E. Charon, *ibid.*, [7] **17**, 250 (1899).