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ALLYLIC OXIDATION OF OLEFINS BY MERCURIC ACETATE (1a-c)

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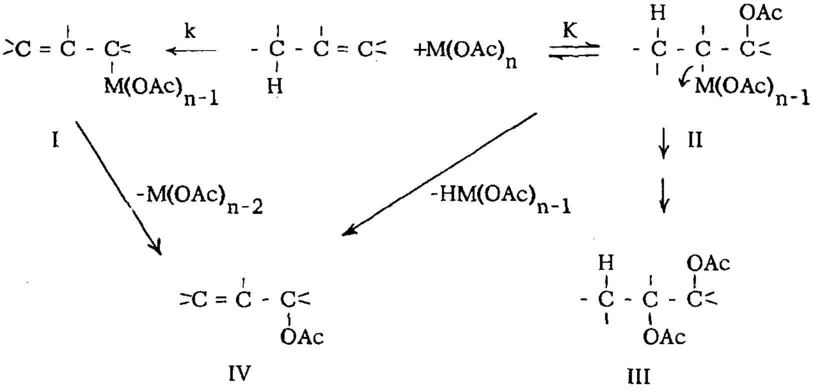
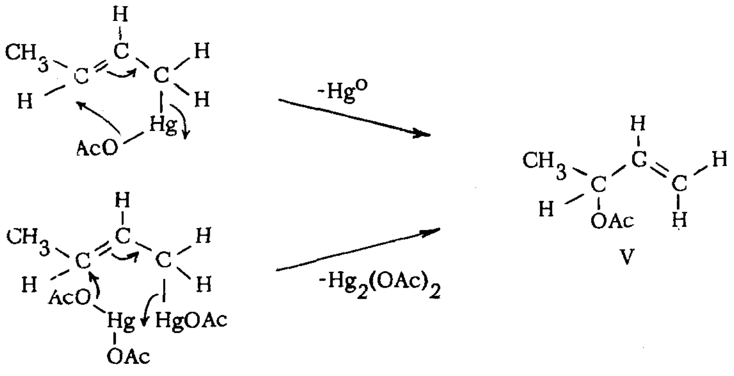
In oxidation of olefins by metal salts, e.g., $M(OAc)_n$ (M = Hg^{II}, Pd^{II}, Tl^{III} and Pb^{IV}), some of the products, e.g., diacetate III, arise from an oxymetalation adduct (2), e.g., II, by reactions involving C-M bond heterolysis. What role the adduct II may also play in the formation of allylic oxidation product IV is far from clear, however. In some cases, allylic oxidation product has been visualized to arise by elimination (2d) of the elements of $HM(OAc)_{n-1}$ from the adduct II (3). On the other hand, allylic organometallic derivatives, e.g., I, are often visualized as intermediates in the allylic oxidation (2d, 4). Developments in our knowledge regarding the nature and behavior of allylic mercurials now permit us to test rather uniquely for their intervention in mercuric acetate oxidation of certain olefins. In this way we can go rather far in elucidating the mechanistic course of this long known allylic oxidation method (3b) in which there has been considerable recent mechanistic interest (5).



In neutral acetic acid solvent butenyl-HgOAc undergoes a "demercuration" reaction (6) of an S_Ni' type to give rise to $\overset{0}{\mathrm{Hg}}$ and pure allylic acetate V, at least 99.5% secondary (> 99.5% S), k for this transformation being ca. 8×10^{-7} $\sec.^{-1}$ at 25°C. The effect of added $Hg(OAc)_2$ is to greatly increase the rate, k being 2.2×10^{-4} $\sec.^{-1}$ at 25°C. in the presence of 0.0565 M $Hg(OAc)_2$. While the inorganic product of this $Hg(OAc)_2$-promoted reaction is now $Hg_2(OAc)_2$, the organic product is still pure V (> 99.5% S). One can visualize a mechanism such as the one symbolized in VI for this $Hg(OAc)_2$-promoted demercuration reaction.



V

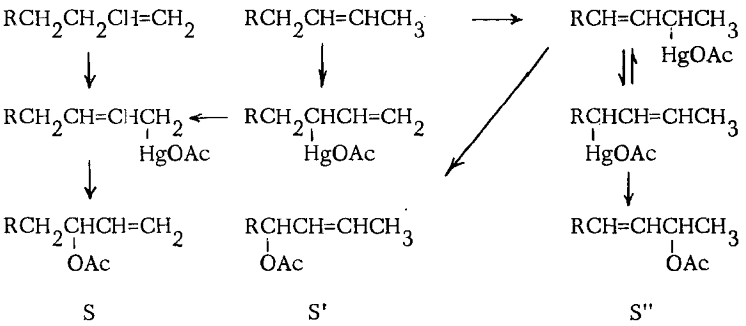
VI

VII; $R = H$ VIIa; $R = H$

VIII; $R = CH_3$ VIIIa; $R = CH_3$

As we have shown elsewhere (7), pure allyl-HgX derivatives in typical solvents such as $CDCl_3$ or DMSO display n. m. r. spectra for ordinary "frozen" σ-allyl structures (VII). However, addition of catalysts, such as HgX_2 salts, now produces the n. m. r. spectra with the AX_4 proton pattern for rapidly equilibrating σ-allyl species VII and VIIa, just as in the case of σ-allyl-MgX (8a), Li (8b) and PdCl (in DMSO) (8c). With the butenyl-HgX system (7), even under conditions for rapid allylic equilibration, the n. m. r. spectra are those for the primary butenyl structure VIII, equilibrium being far on the primary side, just as in the case of the analogous Grignard reagent (8a).

If allylic oxidation of 1- and 2-butene by mercuric acetate in acetic acid proceeds via allylic mercurials, we can anticipate pure secondary acetate V from either butene since any secondary mercurial VIIIa initially formed, e.g., from 2-butene, should rapidly become primary under the reaction conditions and then give rise to secondary acetate. On the assumption that the behavior of the butenyl-HgOAc species VIII and VIIIa is typical of their homologs we would anticipate entirely secondary allylic acetates from other 1- and 2-olefin pairs. With the higher 2-olefins more than one secondary acetate product becomes conceivable, S and S' in the case of 2-pentene and S, S' and S" with the 2-olefins above C_5.



As summarized in Table I, the results of the oxidation of several 1- and 2-olefins with $Hg(OAc)_2$ in AcOH are in agreement with expectations based on an intermediate allylic mercuric acetate. The initial composition of the allylic acetate mixture in the presence of excess olefin is nearly pure secondary ester S, although at equilibrium the primary ester predominates. With cis-2-pentene both S and S' were formed, S' being ca. 20% of the allylic acetates mixture.

As regards other characteristics of the allylic oxidation by $Hg(OAc)_2$, the inorganic product from the oxidation of 1-olefins when the olefin is in excess is metallic Hg (9), and it is $Hg_2(OAc)_2$ in the presence of excess $Hg(OAc)_2$. With 2-olefins, $Hg_2(OAc)_2$ is the inorganic product. The yields of allylic acetates are high, 86-100% being observed for C_5 - C_8 olefins. Small amounts of other monoacetates (possibly enol acetates) were also observed. Diacetates were not observed; e.g., less than 0.4% of 1,2-diacetate was obtained from 1-hexene. Some olefin isomerization was evident by the formation of all the three butenes from the oxidation of either 1- or cis-2-butene at 75°. With three of the 1-olefins studied rough kinetic measurements on the oxidation were

Table I

Allylic Oxidation[a] of Excess C_nH_{2n} by $Hg(OAc)_2$ in AcOH

n	Olefin	%S[b]	Inorg. Prod.[d]	%S[d] at equil.	10^6 k[d] $sec.^{-1}$
4	1-	99.7	Hg	38[e]	1.1 ± 0.1[g]
4	cis-2	97.5(99.0)[c]	$Hg_2(OAc)_2$	35.6[f]; 35.5[e]	
4	trans-2	93.5[d]	$Hg_2(OAc)_2$	38[e]	
5	1-	99.6	Hg	40[e]	1.6 ± 0.1[h]
5	cis-2	98.0 (100.0)[c]	$Hg_2(OAc)_2$	37[f]	
6	1-	97.5 (100.0)[c]	Hg	34[f]	
8	1-	99.6	Hg	32[e]	1.0 ± 0.2[h]

[a] Products were analyzed by vapor phase chromatography and identified by analysis and infrared and n.m.r. spectra. Olefin concentrations 1-4 M, $Hg(OAc)_2$ concentrations 1-3.5 M. [b] At 50°. [c] Extrapolated from %S vs. time curves. [d] At 75°. [e] Allylic acetate distribution obtained on equilibrating mixture of allylic acetates with 0.01-0.05 M $HClO_4$ in AcOH. [f] Final product distribution when the allylic oxidation was conducted with excess $Hg(OAc)_2$. [g] Determined by v.p.c.; $Hg(OAc)_2$ and olefin were in 1:1 ratio. Average of 4 runs in the concentration range 0.07 to 0.74 M. [h] Single run followed gravimetrically by weighing the Hg formed; olefin in excess.

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conducted using either 1:1 mixtures of the two reactants or excess olefin. First order kinetics based on the component with the lower concentration was observed, and the k_1 values are given in Table I.

Although almost pure secondary allylic acetate is formed early in the reaction, and the values in the Table are for early samples, the percentage of the secondary isomer drifts down as the reaction progresses. The drift is more severe with 2- than with 1-olefins. In the presence of excess $Hg(OAc)_2$ this drift is much faster and the composition of the allylic acetate mixture approaches the equilibrium value. These approximate equilibrium values, and the similar ones obtained by subjecting mixtures of allylic acetates to 0.01-0.05 M $HClO_4$

in AcOH are given in Table I. The main cause of the drift is evidently $Hg(OAc)_2$ catalyzed isomerization of the allylic esters, and it could be demonstrated independently that $Hg(OAc)_2$ catalyzes isomerization of crotyl acetate, secondary hexenyl acetate (S) and α-methylallyl acetate. For the latter compound the reaction was followed to equilibrium (10).

The exclusive formation of secondary allylic acetate from both 1- and 2-olefins seems to us to be quite inconsistent with any kind of normal carbonium ion or radical mechanism. Essentially the only way to account for the results is via allylic mercurials which rapidly equilibrate in favor of the primary allylic mercuric acetate and then undergo the unique demercuration to yield secondary acetate (11). The demercuration of the allylic mercurial is considerably more rapid than the olefin oxidation, so that it does not accumulate in the reaction.

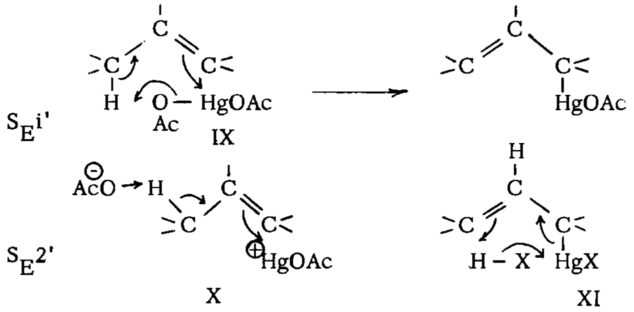
Regarding the kinetics and mechanism of the formation of the allylic mercurial, it should be recognized that acetoxymercuration is rapid, reversible and relatively complete under the allylic oxidation conditions (12). The observed first order kinetics can fit either eq. 1 corresponding to a mechanism involving rate determining oxymercurial decomposition ($k_1 = k$), or eq. 2 for a mechanism involving a rate determining reaction between $Hg(OAc)_2$ and the olefin, both in equilibrium with the oxymercurial, ($k_1 = k/K$). Although the first mechanism has been implied (2a), we prefer the second one, as the reaction rate seems to be too high to be the rate of elimination of acetic acid from a molecule no more activated than is (II). Moreover, k_1 is essentially unchanged when the adduct II has a phenyl group instead of alkyl, i.e., in the oxidation of allylbenzene (13), although this adduct would be expected to be more reactive. This general mechanism is also consistent with the nature of the inorganic product.

The oxymercuration equilibrium is not as far toward adduct with 2-olefins as with 1-olefins. Thus, even with excess 2-olefins, dissociation of the oxymercurial provides enough $Hg(OAc)_2$ for the demercuration of the allylic mercurial to be $Hg(OAc)_2$-promoted (VI). With excess 1-olefin the prevailing $Hg(OAc)_2$ concentration is much lower and presumably unassisted demercuration of the allylic mercurial takes place.

(1) Rate = k [II]

(2) Rate = k [olefin] [$Hg(OAc)_2$] = (k/K) [II]

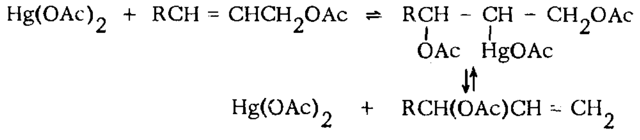
As regards the mode of formation of an allyl organomercurial from the action of $Hg(OAc)_2$ on the olefin, one can visualize either S_Ei' or S_E2' mechanisms along the lines of IX or X. In a general sense, these processes are the microscopic reverse of the previously reported (6) S_Ei' or S_E2' reactions of acids with butenyl-HgX, e.g., XI. These S_Ei' or S_E2' mechanisms may, of course, be elaborated by the inclusion of olefin π-complex or mercurinium ion intermediates (14, 15, 16).



Although, with the present examples of olefins oxidized by $Hg(OAc)_2$, formation of allylic mercurial is followed by generation of pure secondary acetate, this result should not be generalized for widely different olefins. For example, $Hg(OAc)_2$ oxidation of allylbenzene gives rise to the same allylic acetate product as is obtained by demercuration of cinnamyl-HgOAc, so the oxidation apparently involves the cinnamyl-HgOAc as an intermediate (7a, 13). However, in this case, the allylic acetate is a mixture of secondary and primary acetates (7a, 13).

The intervention of allylic mercurial intermediates in allylic olefin oxidation, coupled with their unique behavior, has implications for previous mechanistic tests based on symmetry considerations. Thus, optical activity or isotopic labeling criteria in the oxidation of carvomenthene (2a, 5a) and cyclohexene (5a) have suggested the involvement of a symmetrical intermediate, probably a carbonium ion (5a). While some allylic mercurials under certain conditions do indeed give rise to relatively free carbonium ions, and the mechanism we have described above needn't apply to all allylic oxidations by mercuric acetate, we should note that a "switching" pair of σ-allyl mercurials, even without a carbonium ion intermediate, can give rise to some of the same results as a symmetrical carbonium ion.

We have seen that reversible oxymercuration of the olefin is associated with allylic oxidation by mercuric acetate. In addition, reversible oxymercuration appears to be the probable mechanism of the $Hg(OAc)_2$ catalyzed allylic isomerization of the products. Non-Markovnikov oxymercuration of an allylic acetate followed by deoxymercuration involving the original acetoxy group leads to the allylic isomer of the starting material. This reaction is rather analogous to the mercuric salt catalyzed trans-esterification reaction of vinyl esters with carboxylic acids (17a) or to the closely related trans-etherification (17b, c) for which a similar mechanism has been suggested (17c).



$$\begin{array}{ccc} \mathrm{Hg(OAc)_2 + RCH=CHCH_2OAc} & \rightleftharpoons & \underset{\mathrm{OAc}}{\mathrm{RCH}} - \underset{\mathrm{HgOAc}}{\mathrm{CH}} - \mathrm{CH_2OAc} \\ & & \updownarrow \\ & & \mathrm{Hg(OAc)_2 + RCH(OAc)CH=CH_2} \end{array}$$

The allylic oxidation of olefins by $Hg(OAc)_2$, with its rather unique mechanistic features, represents a useful reference point in the discussion of allylic oxidation by other metal salts (13), e.g., $Tl(OAc)_3$, $Pb(OAc)_4$ and $Pd(OAc)_2$, and we shall report separately on the similarities and differences among these various allylic oxidations. At least some of the features of the mechanism of allylic olefin oxidation by $Hg(OAc)_2$, involving an allylic organometallic derivative undergoing unique demetalation, should be considered in connection with the allylic oxidation of olefins with peresters in the presence of cupric salts (18). With the butenes, for example, this type of oxidation leads so predominantly to secondary allylic ester that an allylic copper species, akin to the allylic mercurial, becomes a plausible intermediate.

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(9) Small amounts of $Hg_2(OAc)_2$ were observed occasionally at the beginning of the reaction, mostly in lower temperature runs.

(10) From reaction of 0.242 M α-methylallyl acetate with 0.294 M $Hg(OAc)_2$ in AcOH at 75° for 23 hrs., 38% of allylic esters were recovered, the composition being 40% S-60% P. The composition of the butenyl acetates at equilibrium in AcOH at 75° is known accurately, being 38.2%S, 10.4%cis-P and 51.4%trans-P. (H. E. Green, Thesis, U. C. L. A., 1965).

(11) Some olefin isomerization in butene oxidation is in agreement with the allylic mercurial intermediate since solvolysis of crotyl-HgOAc gives ca. 14% of a mixture of the three olefins at 75° (7a).

(12) A yellow color, probably due to π-complex, is visible on mixing the olefin and $Hg(OAc)_2$, and it persists until an equimolar amount of olefin is absorbed with the concurrent rapid dissolution of the $Hg(OAc)_2$.

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