## ALLYLIC OXIDATION OF ALLYLBENZENE BY MERCURIC ACETATE Zvi Rappoport<sup>la</sup>, L.K. Dyall<sup>lb</sup>, S. Winstein<sup>lc</sup> and W.G. Young Department of Chemistry, University of California at Los Angeles, California 90024.

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Secondary allylic acetates are the almost exclusive kinetically-controlled products formed in the oxidation of both 1- and 2-olefins by  $Hg(OAc)_2$  in  $AcOH.^2$  A pair of equilibrating primary and secondary allylic mercuric acetates, with the equilibrium being overwhelmingly on the side of the former were suggested as intermediates, based on the exclusive formation of a-methylallyl acetate in the solvolysis of crotyl-HgOAc.<sup>3</sup> The work of Wolfe and coworkers<sup>4</sup> on allylic oxidation of allylbenzene prompts us to publish our results showing that the allylic mercuric acetate is an intermediate in this oxidation too.

The neutral demercuration of 0.01-0.5 M cinnamyl-HgOAc (I) in AcOH at 75° proceeds with a k of ca. 6 x  $10^{-4}$  sec<sup>-1</sup>, giving Hg and a mixture of allylic acetates. Very small amounts of other products containing less than 1% of allylbenzene or 1-phenylpropene were formed.<sup>5</sup>

The kinetically-controlled ratio of the allylic acetates, obtained by extrapolation to zero time, is 40 ± 3% of the secondary ester - a-phenylallyl acetate (II) and 60 ± 3% of the primary ester - cinnamyl acetate (III). The same ratio is obtained also in the presence of  $Hg(OAc)_2$  where the inorganic product is  $Hg_2(OAc)_2$ . The percentage of the PhCH:CHCH\_2HgOAc  $\longrightarrow$  PhCH(OAc)CH:CH<sub>2</sub> + PhCH:CHCH<sub>2</sub>OAc + Hg (I) (III) (III)

secondary isomer decreases rapidly with the progress of the reaction, and the isomerization is faster in the presence of  $Hg(OAc)_2$  probably due to  $Hg(OAc)_2$  catalysis.<sup>2</sup> For the independently measured a-phenylallyl acetate + cinnamyl acetate isomerization  $k_1$ ' at 75° is (2.02 ± 0.10) x 10<sup>-5</sup> sec<sup>-1</sup>.<sup>6</sup> The equilibrium mixture contains > 99.5% of III.

Oxidation of allylbenzene by an equimolar amount of  $Hg(OAc)_2$  in AcOH at reflux for 50 hrs. gave 70% of metallic Hg and a total conversion of 70% from which II(0.5-1.0%), III (96%) and 1,2-diacetoxy-3-phenylpropane (1-2%) were identified.<sup>7</sup> Six additional compounds totalling 2-2.5% were not identified.<sup>8</sup> 1-Phenylpropene was not found although 0.2% could be detected. Quantitative yields of the products were obtained after 1 month at 75°.

Allylbenzene	Hg(OAc)	Hg(OAc)	Inorganic	10 <sup>7</sup> k,
м	M	Allylbenzene	product	sec <sup>-±</sup>
0.78	0.052	0.067	Hg	12.0±0.1
0.10	0.025	0.25	Hg	10.0±0.8
0.10	0.068	0.68	Hg	10.5±1.1
0.20	0.19	0.95	Hg	10.3±1.8
0.01	0.095	0.95	Hg	10.7±1.1
0.08	0.152	1.89	Hg+Hg <sub>2</sub> (OAc) <sub>2</sub>	9.8±0.1
0.01	0.045	4.5	$Hg_2(OAc)_2$	12.4±1.4
	Average $k_1 = (10)$	$0.8 \pm 0.8$ ) x $10^{-7}$ sec	e <sup>-1</sup>	
0.088 <sup>b</sup>	0.038	0.43	Hg	16.6±0.8
0,072°	0.136	1.89	$Hg_2(OAc)_2$	12.7±0.3

Table. Allylic oxidation of allylbenzene by Hg(OAc), in AcOH at 75°.<sup>a</sup>

a The reaction was followed by measuring the concentrations of II and III by v.p.c.

Addition of hydroquinone did not change  $k_1$  or the II/III ratio.

<sup>b</sup> In the presence of 0.76M NaOAc. <sup>c</sup> In the presence of 0.36M NaOAc.

The percentage of II in the allylic acetate mixture after ca 2% reaction at 75° is 36-40%. The same percentage was obtained in the presence of NaOAc.<sup>9</sup> The extrapolated kinetically-controlled distribution was 40±2 II to 60±2 III. A II/III ratio of 35 to 65 was obtained when the adduct of allylbenzene and  $Hg(OAc)_2$  was left for one day at room temperature. Metallic Hg was formed when [Olefin]/[Hg(OAc)\_2] > 1 and Hg<sub>2</sub>(OAc)<sub>2</sub> was formed when [Olefin]/[Hg(OAc)\_2] < 1.

The Table summarizes the rate coefficients for 7 typical runs where the  $Hg(OAc)_2$  to allylbenzene ratio was changed 67-fold. First-order kinetics, based on the component with the lower concentration was observed, and  $k_1$  is reasonably constant irrespective of whether Hg or  $Hg_2(OAc)_2$  were formed. In 20% v/v water-AcOH  $k_1=(12.1\pm1.3) \times 10^{-7} \text{ sec}^{-1}$ , and cinnamyl alcohol constituted less than 5% of the allylic oxidation product.<sup>10</sup>

By using the following scheme and inserting the  $k_1$  and  $k_1'$  values into the corresponding rate equation for consecutive reactions, the percentage of II at the



beginning of the reaction (II)<sub>o</sub> was calculated. The values decrease with the progress of the reaction probably pointing to the operation of an additional isomerization mechanism, <u>i.e.</u>, an  $Hg(OAc)_2$ -catalyzed one.<sup>11</sup> However, extrapolation shows that at the beginning of the reaction  $40\pm3\%$  of the allylic product is  $\alpha$ -phenylallyl acetate.

The similar distribution of the allylic esters obtained in the oxidation of allylbenzene and in the solvolysis of cinnamyl-HgOAc suggests strongly that the cinnamyl-HgOAc is an intermediate in the oxidation. A mechanism, similar to that found in the oxidations with  $Pd(OAc)_2^{12}$ , where HHgOAc is eliminated from IV, requires the formation of enol acetates, but these (e.g.,  $PhCH_2C(OAc):CH_2$ ) were not formed in appreciable amounts. The diacetate results probably from solvolysis of IV with neighbouring acetate participation.

With the solvolysis being 580-times faster than the oxidation the oxidation involves a) a rate determining formation of cinnamyl-HgOAc, and b) a product determining solvolysis of cinnamyl-HgOAc.

The first order kinetics in the oxidation can result either from (i) a rate determining elimination  $(k_E)$  of AcOH from IV, which in turn is formed in a pre-equilibrium (with  $k_1 = k_{eq}/k_E$ ), or by (ii) a concerted  $S_E$ i' reaction of allylbenzene and  $Hg(OAc)_2$  (with  $k_1 = k_D$ ) as symbolised by V. An attractive feature of V is that a "built in" base (the OAc<sup>-</sup> of the AcOHg<sup>+</sup> AcO<sup>-</sup> ion pair) assists in the elimination of the proton. The similar rate coefficients for the oxidation of allylbenzene and 1-butene<sup>2</sup>, and the small effect of NaOAc although  $k_E$  is expected to be accelerated by external base, seem to favour V.



 $Hg(OAc)_2$  is only slightly dissociated in  $AcOH^{4b}$ . In the oxidation of allylbenzene, the covalent  $HgCl_2$  was an inefficient oxidant, and addition of high concentrations of the acetate ion to  $Hg(OAc)_2$  did not change the oxidation rate. An  $AcOHg^+ AcO^-$  ion pair seems therefore to be a likely electrophile in our system.

The product determining demercuration of cinnamyl-HgOAc is the fastest neutral allylic demercuration studied so far. Reactivity order of 80 : 4 : 1 was observed for cinnamyl-, crotyl- and allyl mercuric acetates, respectively. The relative order for the solvolysis of cinnamyl-, crotyl- and allyl chlorides in 50% aqueous ethanol is 8800 : 95 :  $1^{13}$ , suggesting that some kind of carbonium ion is an intermediate in our solvolysis. The formation of considerable amounts of both allylic isomers argues against a cyclic  $S_N$ ' mechanism, contrary to that found for crotyl-HgOAc. The solvolysis of the allylic mercurials is therefore an additional example for the spectrum of ion pairs and cyclic mechanisms in allylic reactions.

The kinetically-controlled solvolysis products are richer in the more stable primary isomer as found also for the AgOAc-catalyzed solvolysis of the butenyl halides in AcOH.<sup>14</sup> Either solvent participation in the solvolysis, or little discrimination between the two positive centers of the allylic carbonium ion in AcOH may be responsible for this.<sup>15</sup> The AgOAc-catalyzed solvolysis of cinnamyl chloride gives a very similar distribution of the allylic acetates at room temperature<sup>16</sup> and a similar intermediate may participate in both reactions.

The role of  $\text{Hg(OAc)}_2$  in increasing the demercuration rate is not clear. As the II/III ratio remains the same as in the neutral solvolysis, the most plausible mechanism is an electrophilically-promoted solvolysis by attack on the mercury atom of the cinnamyl-HgOAc. The formation of  $\text{Hg}_2(\text{OAc})_2$  in this reaction suggests that this is the reason for its formation in allylic oxidations with excess  $\text{Hg(OAc)}_2$ .

That cinnamyl-HgOAc forms very little olefin on solvolysis has a bearing on Wolfe's conclusions regarding the mechanism of allylic oxidation with  $Hg(OAc)_2$ .<sup>3b</sup> Wolfe rules out cyclohexenyl-HgOAc as the intermediate in cyclohexene oxidation owing to the absence of hydrogen exchange with the solvent in the recovered cyclohexene. He noted that this conclusion would be invalidated if only small amounts of olefins were formed in the solvolysis of cyclohexenyl-HgOAc, which could not be prepared. Our results show formation

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of 80, 16 and < 1% of olefins on solvolysis of allyl-, crotyl- and cinnamyl mercuric acetates, respectively, <u>i.e.</u>, less olefin with higher carbonium ion stability. Hence, solvolysis of cyclohexenyl-HgOAc, which can be assumed to be more reactive than crotyl-HgOAc, would give only small amounts of cyclohexene, and little exchange.

An oxidation with cinnamyl-HgOAc as an intermediate appears reasonable but not compelling to Wolfe, as no rearranged olefin and no more than 2% of II were observed. Calculations using  $k_1$  and  $k_1'$  predict that at 75° the <u>maximum yield</u> expected for II is 4.6% and Wolfe's lower yield is due either to the higher temperature used, or from observing the yields not at their maximum value. Wolfe, as Wiberg had done earlier,<sup>17</sup> based his argument for a symmetrical intermediate on the formation of equal amounts of isomeric allylic acetates in the oxidation of a symmetrical olefin (e.g. cyclohexene). However, such considerations may be misleading if the metal salt-catalyzed allylic isomerization<sup>2</sup> is not taken into account. While all the mechanisms suggested so far for Hg(OAc)<sub>2</sub>-oxidation predict equal amounts of the two isomers in oxidations of symmetrical olefins, in oxidations with other metal acetates, e.g., Pd(OAc)<sub>2</sub><sup>12</sup> a neglect of the allylic isomerization would lead to an erroneous conclusion regarding the oxidation mechanism.

## References

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- 2. Z. Rappoport, P.D. Sleezer, S. Winstein and W.G. Young, Tet.Lett., 3719 (1965).
- 3. P.D. Sleezer, S. Winstein and W.G. Young, J.Amer.Chem.Soc., 85, 1890 (1963).
- (a) S. Wolfe and P.G.C. Campbell, <u>Can.J.Chem.</u>, <u>43</u>, 1184 (1965); (b) S. Wolfe,
  P.G.C. Campbell and G.E. Palmer, <u>Tet.Lett.</u>, 4023 (1966).
- 5. With 0.08-1M concentrations of cinnamy1-HgOAc both Hg and Hg<sub>2</sub>(OAc)<sub>2</sub> are formed and additional organic compounds (some of which disappear rapidly during the reaction) appear. However, the main products are II and III in ca. 40 : 60 ratio.
- 6.  $k_1'$  is little affected by adding NaOAc. In the presence of 0.8M NaOAc  $k_1' = (2.41 \pm 0.12) \times 10^{-5} \text{ sec}^{-1}$ .

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- 7. Identification was made by comparing the I.R., N.M.R., refractive index and v.p.c. retention time with those of authentic samples.
- 8. The main compound (1-2% of the total) showed an ester C:0 in the I.R. and is also formed in the reaction of II and III with  $Hg(OAc)_2$ .
- 9. E.g., oxidation of 0.46M allylbenzene by 0.05M Hg(OAc)<sub>2</sub> at 75° for 150 min. gave 40% and 37% of II/(II+III) without and with 0.6M NaOAc, respectively.
- 10. Isomerization is faster in this medium. E.g., 0.5% II was found after 23 hours in 20% v/v water-AcOH compared to 16% after 20 hours in AcOH.
- 11. Control experiments showed that salt effects are unlikely cause for this phenomenon.
- W. Kitching, Z. Rappoport, S. Winstein and W.G. Young, <u>J.Amer.Chem.Soc.</u>, <u>88</u>, 2054 (1966).
- 13. C.A. Vernon, J.Chem.Soc., 423, 4462 (1954).
- 14. J.D. Roberts, W.G. Young and S. Winstein, <u>J.Amer.Chem.Soc.</u>, <u>64</u>, 2157 (1942).
- R.H. DeWolfe and W.G. Young in "The Chemistry of Alkenes" (Ed. S. Patai), Interscience, London, 1964, p.681.
- 16. J. Meisenheimer and J. Link, Ann., 479, 211 (1930).
- 17. K.B. Wiberg and S.D. Nielsen, J.Org. Chem., 29, 3353 (1964).