Oxidation of Olefins by Palladium(II). 12.[1] Product Distributions and Kinetics of the Oxidation of 3-Buten-2-ol and 2-Buten-1-ol by $PdCl_4^{2-}$ in Aqueous Solution

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The rate expression for oxidation of both allyl alcohols was determined to be rate = $k[PdCl_4^{2-}][C_3H_6O]/[H^+][Cl^-]^2$, an expression identical in form with that found previously for the oxidation of ethene, allyl alcohol, and other acyclic olefins, indicating similar mechanisms. Contrary to previous reports, the product distribution from 3-buten-2-ol (**6**) was completely different from that for 2-buten-1-ol (**7**), indicating that fast isomerization into an equilibrium mixture before oxidation was not occurring. A short study of the rate of isomerization using deuteriated **6** and **7** confirmed that isomerization was slow under the oxidation conditions. The distributions gave considerable information on the effects of steric and electronic factors on the modes of hydroxypalladation. While allyl alcohol gave a 3/1 preference for addition of the Pd(II) to the center carbon due to the directing influence of the hydroxyl group, **6** gave a 4/1 preference for addition of the Pd(II) to the end carbon. The steric effect of the methyl is thus appreciable. With **7** the double bond is internal so steric factors are not important and the directing influence of the hydroxyl will be the important effect. The ratio of Pd(II) addition next to the carbon containing the hydroxyl group to addition to the other side of the double bond is 34/1, indicating considerable directing influence of the hydroxyl. The preference for secondary over primary hydride shift is 1.25, a value which indicates almost no carbonium ion character and considerable Pd(II)-H character. Using a specifically deuteriated **7**, the value of the deuterium isotope effect, k_H/k_D, can be determined by internal competitive hydride transfer by taking into account the positional preferance for secondary hydride shift. This value of 2.2 is close to values previously determined for ethene and allyl alcohol.

Introduction

The rate expression for the oxidation of acyclic olefins by aqueous $PdCl_4^{2-}$ to aldehydes and ketones (eq 1) follows the rate expression given by eq 2. It is generally agreed

$$PdCl_4^{2-} + C_nH_{2n} + H_2O \rightarrow Pd(0) + C_nH_{2n}O + 2HCl + 2Cl^- \quad (1)$$

$$\frac{-d[\text{olefin}]}{dt} = \frac{k[PdCl_4^{2-}][\text{olefin}]}{[H^+][Cl^-]^2} \quad (2)$$

that the mechanism involves conversion of an olefin π-bonded to palladium(II) to a palladium(II) 2-hydroxyalkyl species (**1**), a process called hydroxypalladation.[2] As shown in eq 3, with α-olefins the hydroxypalladation can occur in either a Markovnikov fashion to give **1a** or in a non-Markovnikov fashion to give **1b**.

$$CH_2{=}CHR + Pd(II) + H_2O \xrightarrow{-H^+} \underset{\mathbf{1a}}{Pd(II)CH_2CH(OH)R} + \underset{\mathbf{1b}}{HOCH_2CH(Pd(II))R} \quad (3)$$

The last two papers in this series have described the products[3] and kinetics[1] of oxidation of allyl alcohol by aqueous palladium(II) chloride. The oxidation products were $HOCH_2CH_2CHO$ (**2**), $CH_3C(=O)CH_2OH$ (**3**), and acrolein (**4**). The main product, **2**, resulted from decomposition by hydride shift of an intermediate analogous to **1b** (R = CH_2OH) while **3** was formed in an analogous fashion from an intermediate analogous to **1a**. The acrolein did not result from an hydroxypalladation adduct such as **1**, but rather by direct hydride abstraction from the alcohol carbon.[3] The kinetics of oxidation of allyl alcohol obeyed eq 2, indicating its mechanism of oxidation is similar to other acyclic olefins. One important result of this work was the demonstration that the deuteriated allyl alcohols, $CH_2{=}CHCD_2OH$ (**5a**) and $CD_2{=}CHCH_2OH$ (**5b**), did not isomerize into an equilibrium mixture of each during the course of the oxidation. This result indicated that hydroxypalladation was not reversible for, if it were, the isomerization would have occurred through the deuteriated hydroxypalladation derivative of **1b**, $HOCD_2CH(Pd(II))CH_2OH$.

The oxidation of 3-buten-2-ol (**6**) and 2-buten-1-ol (**7**) is of interest for several reasons. First, it has been reported that the two alcohols are rapidly isomerized into an equilibrium mixture under the reaction conditions and thus both give the same products, $CH_3C(=O)CH{=}CH_2$ and $CH_3CH{=}CHCHO$, believed to arise from dehydration of the initial hydroxycarbonyl products.[4] In light of the results with allyl alcohol indicating a lack of allylic isomerization, this system merits reinvestigation. Second, a knowledge of the product distribution will give data on the relative tendencies for hydride transfer from primary carbon atoms as compared with secondary carbon atoms. This information in turn will allow inferences concerning the degree of carbonium ion character in the transition state for decomposition of the hydroxypalladation intermediates. Third, a knowledge of the product distribution will also give information on the magnitudes of steric and electronic effects on the direction of hydroxypalladation. In particular information on the importance of the non-Markovnikov directing influence of hydroxyl should be forthcoming. Fourth, deuterium isotope effects for the hydride shifts can be determined using deuteriated alcohols, and these isotope effects can be compared with those previously determined for ethylene[5,6] and allyl alcohol.[3] Fifth, the rate expression for the oxidation of these alcohols should be measured to see if it agrees with eq 2, indicating

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(2) For general discussion and references, see: Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, Holland, 1980; pp 41-84.
(3) Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1985**, *4*, 1286.
(4) Jira, R. *Tetrahedron Lett.* **1971**, 1225.
(5) Henry, P. M. *J. Org. Chem.* **1973**, *38*, 2415.
(6) (a) Kosaki, M.; Isemura, M.; Kitaura, K.; Shinoda, S.; Saito, Y. *J. Mol. Catal.* **1977**, *2*, 351. (b) Saito, Y.; Shinoda, S. *J. Mol. Catal.* **1980**, *9*, 461.

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Table I. Summary of Kinetic Runs[a]

run	$[PdCl_4^{2-}]$	$[H^+]$[b]	$[Cl^-]$[c]	10^5k_{obsd}, s^{-1}		10^4k,[d] M^2 s^{-1}	
				6	7	6	7
1	0.005	0.2	0.6	1.2	0.52	1.7	0.75
2	0.0125	0.2	0.6	2.4	1.7	1.4	0.95
3	0.025	0.2	0.6	4.6	2.7	1.3	0.78
4	0.050	0.2	0.6	10.	5.1	1.4	0.73
5	0.025	0.2	0.4	8.9	5.1	1.1	0.66
6	0.025	0.2	0.9	2.4	1.5	1.6	0.97
7	0.025	0.2	1.2	1.7	0.77	2.0	0.89
8	0.025	0.4	0.6	2.1	1.6	1.2	0.92
9	0.025	0.6	0.6	1.4	1.2	1.2	1.0
10	0.025	0.8	0.6	1.2	0.84	1.4	0.97
					av	1.4	0.87

[a] All runs are in aqueous solution at 25 °C. $LiClO_4$ was added to bring the ionic strength to 2.0. Initial allyl alcohol and quinone concentrations are 0.005. Data is treated as a first-order reaction in allyl alcohol. **6** is 3-buten-2-ol and **7** is 2-buten-1-ol. Each rate constant is the average of at least two runs which agreed within 15%. [b] Added as $HClO_4$. [c] Added as LiCl. [d] Calculated assuming the rate expression given by eq 2 is operative.

these substituted allyl alcohols behave in a fashion similar to other acyclic olefins. In addition the values of the rate constants will give information in regard to the effect of structure on rate and also provide an interesting comparison with other acyclic olefins.

Results

Yields and Product Distributions. All yields and product distributions were determined at 25 °C under the conditions: $[Pd(II)] = [H^+] = [Cl^-] = 0.1$ M. The reactions were usually run for 30 min. The distributions given are the average of at least four determinations. One problem that arose was the fact one product expected from crotyl alcohol, **7**, 3-hydroxybutanal, **8**, dehydrates into another expected product, crotonaldehyde, **9**, in the presence of acid and base.[7] In order to prevent this dehydration the 2,4-DNP derivative was prepared at 2 °C. Control experiments using authentic **8** demonstrated that under these conditions at least 95% of **8** could be recovered without dehydration.

Yields of carbonyl products were determined by an oximation procedure which gave total products. The total yield of carbonyl products based on palladium(0) formed was 90% for 2-buten-1-ol and 96% for 3-buten-2-ol.

The product distribution for the oxidation of 3-buten-2-ol is given in eq 4 (Q = *p*-benzoquinone).

The product distribution for the oxidation of 2-buten-1-ol is given in eq 5.

$$\underset{\mathbf{6}}{CH_2{=}CHCH(OH)CH_3} \xrightarrow[HCl,\ Q]{PdCl_4^{2-}} \underset{\mathbf{10}\ (79\%)}{CH_3C(=O)CH(OH)CH_3} + \underset{\mathbf{8}\ (8\%)}{CH_3CH(OH)CH_2CHO} + \underset{\mathbf{11}\ (10\%)}{CH_2(OH)CH_2C(=O)CH_3} + \underset{\mathbf{12}\ (0.7\%)}{CH_2{=}CHC(=O)CH_3} + \underset{\mathbf{9}\ (2.3\%)}{CH_3CH{=}CHCHO} \quad (4)$$

$$\underset{\mathbf{7}}{CH_3CH{=}CHCH_2OH} \xrightarrow[HCl,\ Q]{PdCl_4^{2-}} \underset{\mathbf{11}\ (49\%)}{CH_2(OH)CH_2C(=O)CH_3} + \underset{\mathbf{8}\ (39\%)}{CH_3CH(OH)CH_2CHO} + \underset{\mathbf{13}\ (2.6\%)}{CH_2(OH)C(=O)CH_2CH_3} + \underset{\mathbf{9}\ (8.5\%)}{CH_3CH{=}CHCHO} + \underset{\mathbf{12}\ (0.9\%)}{CH_2{=}CHC(=O)CH_3} \quad (5)$$

Deuterium Labeling. The deuterium labeled crotyl alcohol, **7′**, was used to determine the isotope effect for hydride shift. The alcohol, **7′**, was oxidized under the same conditions as **7** itself and the ratio **11′**/**8′** determined by a combination of ^1H and ^2H NMR analyses. As shown in eq 6 the ratio was found to be 2.8.

$$\underset{\mathbf{7'}}{CH_3CH{=}CHCD_2OH} \xrightarrow[HCl,\ Q]{PdCl_4^{2-}} \underset{\mathbf{8'}\ (1.0)}{CH_3CH(OH)CHDCDO} + \underset{\mathbf{11'}\ (2.8)}{CH_3C(=O)CH_2CD_2OH} \quad (6)$$

Kinetics. All kinetic runs were carried out at 25 °C in the presence of *p*-benzoquinone (Q) which reoxidized the Pd(0) formed back to Pd(II) while being reduced itself to hydroquinone (H_2Q) so the reaction was catalytic in Pd(II) and the formation of π-allylic palladium(II) species was avoided. The reaction is shown in eq 7. The kinetics were studied using a potentiometric procedure based on the quinone–hydroquinone redox couple. Lithium salts were used for the kinetic runs and the ionic strength was maintained at 2.0 using lithium perchlorate as inert electrolyte.

$$H_2O + C_4H_8O + Q \xrightarrow{Li_2PdCl_4} C_4H_8O_2 + H_2Q \quad (7)$$

The data is summarized in Table I. Runs 1–4 test the effect of palladium(II) concentration while runs 3 and 5–7 determine the order in $[Cl^-]$ and runs 3 and 8–10 determine the order in $[H^+]$. The fact that the values of k calculated assuming a rate expression of the form of eq 2 remain relatively constant indicate this rate expression is indeed the correct one with values of k of 1.4×10^{-4} M^2 s^{-1} for 3-buten-2-ol and 8.7×10^{-5} M^2 s^{-1} for 2-buten-1-ol.

A short study of the isomerization of each of the two allyl alcohols into each other was undertaken. Under the conditions where the oxidation reaction was very slow ($[Pd(II)] = 0.05$ M, $[Cl^-] = 1.6$ M, $[Q] = 0.1$ M, $[H^+] = 0.2$ M), $CH_3CH{=}CHCD_2OH$ (**7′**) gave 5–7% of $CH_3CHOHCH{=}CD_2$ while $CH_3CDOHCH{=}CH_2$ (**6′**) gave 5–7% of CH_3C-$D{=}CHCH_2OH$ in 2 h. From studies of the isomerization of the deuteriated allyl alcohol itself, the rate expression would be expected to be that given by eq 8 (AA = allyl alcohol).[8] The amount of isomerization given above

$$\frac{-d[AA]}{dt} = \frac{k_i[PdCl_4^{2-}][AA]}{[Cl^-]} \quad (8)$$

corresponds to a value of k_i in eq 8 of $\sim 5 \times 10^{-4}$ s^{-1}. Under the conditions of the product distribution the rate of oxidation was about 20 times that of isomerization, so the product distribution would not be expected to be greatly affected by isomerization. In fact, only one product gave

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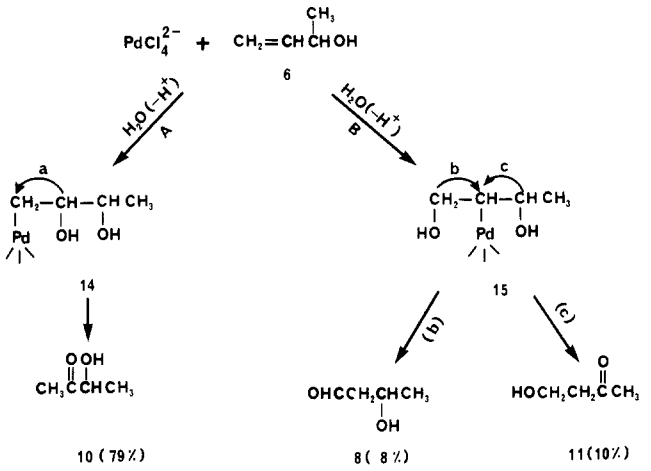
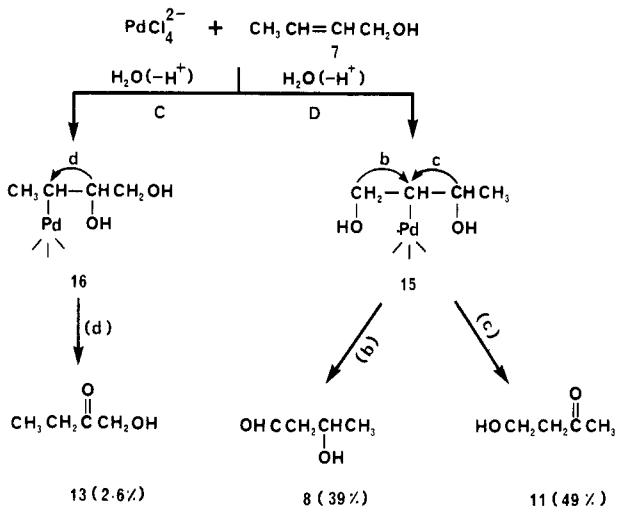
Scheme I



Scheme II



any evidence of isomerized allylic alcohol. The product **10**, by far the major product from 3-buten-2-ol, **6**, was found in the oxidation products from oxidation of crotyl alcohol, **7**, to the extent of a few percent when the oxidation was run for the standard 30 min. Of course the hydroxypalladation mechanism would not predict **10** to be an initial product from **7** so it must have arisen from **6** formed by isomerization of **7**. The fact that **10** was not an initial oxidation product from **7** was demonstrated by reducing the reaction time to 10 min. The proportion of **10** in the oxidation products decreased by a factor of 4 indicating it was being formed by oxidation of **6** produced by isomerization. The product distribution for **6** was corrected, assuming **10** was *not* an initial oxidation product.

Discussion

As expected from previous results with deuteriated allyl alcohol,[3] 3-buten-2-ol and crotyl alcohol gave quite different product distributions. These product distributions can be explained by a combination of steric and electronic effects which direct the mode of hydroxypalladation and electronic effects which determine hydride shift preferences. Based on previous results the predicted reaction pathway for 3-buten-2-ol is shown in Scheme I while that for crotyl alcohol is shown in Scheme II.[2]

The point to be made is that, if hydroxypalladation–dehydroxypalladation were much more rapid than oxidation, **6** and **7** would be rapidly isomerized into an equilibrium mixture through the common hydroxypalladation intermediate, **15**, and the product distributions for both would be the same. Fortunately, as expected from the results with allyl alcohol, this is not the case, so it is possible to gain mechanistic insight regarding the factors important in palladium(II) catalysis from the individual product distributions.

First, in regard to factors affecting mode of hydroxypalladation, 3-buten-2-ol is an α-olefin and in analogy with other α-olefins would be expected to give ketone products by a Markovnikov mode of addition (path A in Scheme I). Thus steric factors, which favor putting the large Pd(II) and its ligands on the less hindered end carbon, predominate. However the preference for Markovnikov addition is not large since the ratio, **10**/(**8** + **11**), is 4.4. For propene the ratio of acetone, which corresponds to **10**, to propanal, which corresponds to **8** + **11**, is about 9.[9a] However, as discussed below, the directing influence of the hydroxyl group opposes Markovnikov addition. It is interesting to compare 3-buten-2-ol with allyl alcohol itself where the ratio of path A to path B is 1/3 or the reverse found for **6**.[3] Not unexpectedly the extra methyl group adds appreciable steric hindrance to path B. In contrast, for crotyl alcohol, **7**, since the double bond is internal, steric factors would be much less important in determining mode of addition, and the directing influence of the hydroxyl group would be expected to become the predominant factor. Apparently the directing power of the hydroxyl group is considerable since the ratio of products (**8** and **11**) arising from path D in Scheme II to the product (**13**) arising from path C is 34. As mentioned previously the ratio for allyl alcohol is 3, but in that case steric factors opposed the pathway arising from non-Markovnikov addition. The directing influence of the hydroxyl group could result strictly from its electron-withdrawing properties, and such substituents do promote non-Markovnikov addition.[9] However it could partially result from hydrogen bonding to the chloride ligands of the Pd(II). This type of directing influence has been suggested for Pd(II) reactions with allyl alcohols.[10] Of course the latter directing influence would also effect the stereochemistry of the products in some systems. Thus, in order to confirm the hydrogen-bonding mechanism, either cyclic or chiral allylic alcohols would have to be studied. Recent results with both cyclic[11] and chiral[12] systems indicate that the hydrogen bonding is, in fact, an important factor.

The tendency for hydride shift can be determined from the ratio of the products resulting from the common intermediate, **15**, which is formed from both allylic alcohols. Although the yields of **8** and **11** differ considerably in the two reaction mixtures, in both the ratio, **11**/**8**, is 1.25 ± 0.05. This result indicates a slight preference (2.5 if the statistical factor of two is taken into account) for hydride shift from a secondary alcohol carbon as opposed to a primary alcohol carbon. For a hydride shift involving carbonium ion character, secondary carbon hydride shift would be perferred over primary carbon hydride shift by factors of 4 to 70.[13-16] Probably the best comparison is

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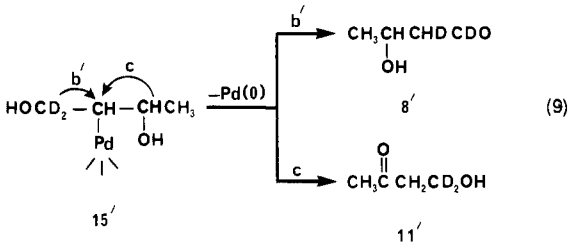
(10) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896.
(11) Wan, W. K.; Zaw, K. unpublished results.
(12) Smadja, W.; Czernecki, S.; Ville, G.; Georgoulis, C. *Organometallics* **1987**, *6*, 166.
(13) Cannell, L. C.; Taft, R. W. *J. Am. Chem. Soc.* **1956**, *78*, 5812.
(14) Cowan, H. D.; McCabe, C. L.; Warner, J. C. *J. Am. Chem. Soc.* **1950**, *72*, 1194.
(15) Gregor, I. K.; Riggs, N. V.; Stimson, V. R. *J. Chem. Soc.* **1956**, 76.

the oxidation of propene and ethene, respectively, by aqueous thallic ion.[16] These oxidations proceed through hydroxythallation adducts analogous to those proposed for aqueous palladium(II) oxidations of the same olefins. However in the thallic ion oxidations there is a competition between decomposition of the intermediate by hydride shift to give carbonyl products or attack of water to give glycol. The preference for secondary over primary hydride shift is about four in this system. The decomposition of the adduct involves a transition state with considerable carbonium ion character. The low value found for the hydride shift preference found in this work is almost certainly a reflection of a hydride shift transition state with little or no carbonium ion character but with considerable Pd(II)–H bond character. It is generally agreed that the reason no glycol products are formed in the decomposition of intermediates such as **15** is due to the fact that discrete Pd(II)–H species are present as intermediates in the hydride transfer.[17,18] The formation of these hydrides would not be expected to have as large a primary versus secondary site preference as would a carbonium ion transition state.

The deuterium isotope effect measured with **7′** is a measure of the relative tendencies of hydride vs deuterium shift in the decomposition of **15′** as shown in eq 9. The



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ratio of path c to path b′, which is an apparent deuterium isotope effect, was found to be 2.8. This value is somewhat higher than the value found for ethene and allyl alcohol. However in the previous cases there was no inherent site preference for hydride transfer since both hydroxyls were on primary carbons. However, in the hydroxypalladation intermediate, **15′**, one hydroxyl is on a primary carbon and the other on a secondary carbon so there is a site preference which must be taken into account. In order to obtain the true isotope effect the value of the apparent isotope effect must be divided by the site preference of path c over path b′. Since this preference is 1.25 ± 0.05 the real deuterium isotope is then $k_H/k_D = 2.8/1.25 = 2.2 \pm 0.1$, which is close to the value of 1.9 ± 0.1 found previously for ethene[5,6a] and allyl alcohol.[3] The deuterium isotope effect is thus independent of structure when corrected for the site preference for hydride shift.

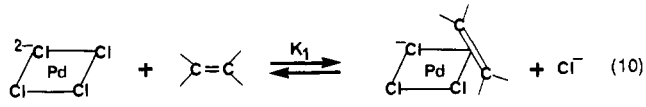
The formation of the allylic ketones **9** and **12** is of interest because previously it was reported that allyl alcohol as well as **6** and **7** gave only allylic ketones which were acrolein in the case of allyl alcohol and the same mixture of **9** and **12** in the oxidation of either **6** or **7**.[4] It was suggested that they arose from dehydration of the initial hydroxy ketone products and **6** and **7** isomerized into an equilibrium mixture before oxidation so both gave the same product distribution. However, in the allyl alcohol oxidation, deuterium-labeling experiments demonstrated that the acrolein arose from direct hydride extraction from the alcohol carbon and the isomerization of one deuteriated allyl alcohol into the other isomer was very slow under the usual oxidation conditions. The present results are of interest in comparison with those for allyl alcohol. Allyl alcohol gave a 30% yield of acrolein. It is noteworthy that the yields of these products are appreciably lower in the case of the substituted allyl alcohols. In the case of crotyl alcohol the yield of crotonaldehyde, **9**, is 8.5%, much more than can be explained by dehydration of **8** (<2%), but less than 1/3 of that from allyl alcohol. Although the deuterium-labeling experiments were not performed with **9**, presumably both involve abstraction from a primary carbon. This factor could result from the lower stability of the olefin π-complex with **9** as compared with allyl alcohol, thus providing less opportunity for H-abstraction. The small amounts of **12** are probably not significant. They could result from some dehydration of **11**, the major saturated product. However the distribution of **9** and **12** with 3-buten-2-ol, **6**, is unexpected. The major unsaturated ketone, **9**, in 2.3% yield could not have arisen by direct hydride abstraction, and the expected unsaturated ketone, **12**, is present to the extent of only 0.7%. Some of the **9** would arise from dehydration of **8**, but this amount would be expected to be no more than 0.4% (8% × 0.05). π-Allylic species are a possibility but, because of the small amounts of **9** involved, they could not be very important reaction intermediates. Most surprising is the low yield of **12**, which must mean that direct hydride abstraction from a secondary alcohol carbon is not a very favorable process.

Table II. Values of K_1, k', and k for Several Acyclic Olefins[a]

olefin	K_1	$10^5k'$, M^2 s^{-1}	10^4k, M^2 s^{-1}
ethene	17.4	20.3	35.0
propene	14.5	6.5	9.4
cis-2-butene	8.7	3.5	3.0
trans-2-butene	4.5	7.5	3.4
1-butene	11.2	3.5	3.9
allyl alcohol	5.0	8.0	4.0
2-buten-1-ol			0.87
3-buten-2-ol			1.4

[a] μ = 2.0 (adjusted with $LiClO_4$ or $NaClO_4$).

The kinetic studies provides useful information concerning the behavior of allylic alcohols in comparison with other acyclic olefins. The fact that crotyl alcohol and 3-buten-2-ol obey the same rate expression as other acyclic olefins is convincing evidence that all are oxidized by similar mechanisms. Also the fact that isomerization of one allylic alcohol into the other is slow compared with the rate of oxidation supports earlier work with allyl alcohol itself but does not add any new information.[1] The absolute values of the rate constants are also of interest for comparison purposes. In regard to the relative rates of **6** and **7**, it would be expected that the α-olefin might be the fastest because it has the least hindered double bond. As the data in Table I shows, this is in fact the case but the difference is not very pronounced since the increase is only a factor of 1.6. The reason for this small difference is related to the form of the rate constant k in eq 1. It is actually a composite of an equilibrium constant, K_1, and a rate constant, k'. K_1 is the equilibrium constant for the equilibrium given in eq 10 and k' is the rate constant for reaction of **17** to give oxidation products. Since K_1 has the



(10)

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form given by eq 11 the rate equation given by eq 2 can be rewritten in the form given by eq 12. Thus $k = K_1k'$ and the overall rate constant, k, will be influenced by the effect of structural changes on both K_1 and k'. Kinetic

$$K_1 = [17][Cl^-]/[PdCl_4^{2-}][olefin] \quad (11)$$

$$\frac{-d[olefin]}{dt} = \frac{k'[17]}{[H^+][Cl^-]} = \frac{k'K_1[PdCl_4^{2-}][olefin]}{[H^+][Cl^-]^2} \quad (12)$$

data for several acyclic olefins studied in these laboratories is given in Table II.[11,19] Considering the isomeric butene series, it can be seen that as K_1 increases the value of k' tends to decrease so the value of k changes little. The reason for this effect is that as the stability of the intermediate π-complex increases (larger K_1) there is less tendency for it to react further to undergo hydroxypalladation (lower k').[20] Thus, in going from *trans*-2-butene to 1-butene, the value of K_1 increases by a factor of ~2.5 while the value of k decreases by a factor of more than 2. The net result is that the value of k for 1-butene is only 15% higher than the k for *trans*-2-butene. Although, because of the difficulties in measuring π-complex formation constants with liquid olefins under oxidation conditions, K_1's were not measured in the present study, similar effects are no doubt operative for the two allyl alcohols, **6** and **7**. Thus a higher value of K_1 for 3-buten-2-ol is offset by a lower value of k' as compared with 2-buten-1-ol. The net result is that k is similar for the two alcohols.

Another comparison is the values of K_1, k', and k for the allylic alcohols and their hydrocarbon counterparts. The most detailed comparison can be made between allyl alcohol and propene since all three values are known for both. The lower value of K_1 for allyl alcohol is expected since it is known that electron-withdrawing groups decrease K_1.[22] This is compensated by only a small increase of k' for allyl alcohol over that for propene so the k for propene is ~2.4 times that for allyl alcohol. Thus the decrease in K_1 is not compensated for by a corresponding increase in k' and allyl alcohol has a smaller value of k than the corresponding hydrocarbon. The same trends apply to the two allyl alcohols in the present study. The k for 1-butene is ~2.4 times that for 3-buten-2-ol, so this result is exactly what would be expected on the basis of the above comparison. The biggest difference is for 2-buten-1-ol. The value of k for *trans*-2-butene is ~4 times that for this allylic alcohol or a little lower than expected of the above analysis. However, in general the trends in rate do not deviate greatly from that expected from the propene–allyl alcohol comparison and thus the allylic alcohols, **6** and **7**, appear to behave in a normal fashion.

Finally, none of the simple saturated carbonyl products, butanal and 2-butanone, were detected in this work, although significant amounts of propanal were found in the allyl alcohol oxidation.[3] The reason may simply be that the secondary reduction is not as important with the more hindered olefins. In any case the saturated carbonyls would be more difficult to detect because of the lower yields of **9** and **12**.

(19) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595.

(20) This effect has been found in at least one other system. In the oxidation of substituted styrenes in acetic acid by palladium(II) acetate (see ref 2, p 186–187), it was found that the value of K_1 increased as the electron-donating power of the aromatic substituent increased. However this was almost exactly compensated by a decrease in k' so the value of k remained practically constant.[21]

(21) Lee, H.-B.; Mizukami, F., unpublished results.

(22) Ban, E.; Hughes, R. P.; Powell, J. *J. Chem. Soc., Chem. Commun.* **1973**, 591; *J. Organomet. Chem.* **1974**, *69*, 455.

Table III. ^{1}H NMR (300-MHz) of (2,4-Dinitrophenyl)hydrazone Derivatives of Carbonyl Products[a]

derivative	proton	chemical shifts,[b] ppm
$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}(CH_3)$=NNHAr	H_a	1.2 (t, J_{ab} = 7.4 Hz, 3 H)
	H_b	2.5 (q, J_{ab} = 7.4 Hz, 2 H)
	H_c	2.1 (s, 3 H)
$\overset{a}{C}H_3\overset{b}{C}H=\overset{c}{C}H\overset{d}{C}H$=NNHAr	H_a	2.0 (d, J_{ab} = 5.9 Hz, 3 H)
	$H_{b,c}$	6.3 (m, $J_{ab,cd}$ ~ 5.8, 11.7 Hz, 2 H)
	H_d	7.7 (d, J_{cd} = 8.4 Hz, 1 H)
$\overset{a}{C}H_2=\overset{b}{C}H\overset{c}{C}(CH_3)$=NNHAr	H_a	5.7 (m, J_{ab} ~ 1.8, 11.1 Hz, 2 H)
	H_b	6.6 (m, J_{ab} ~ 1.8, 11.1 Hz, 1 H)
	H_c	2.2 (s, 3 H)
$\overset{a}{C}H_3\overset{b}{C}H(OH)\overset{c}{C}H_2\overset{d}{C}H$=NNHAr	H_a	1.2 (d, J_{ab} = 6.4 Hz, 3 H)
	H_b	4.2 (m, $J_{ab,bc}$ ~ 6.2–6.5 Hz, 1 H)
	H_c	2.5 (m, $J_{bc,cd}$ ~ 4.8–5.2 Hz, 2 H)
	H_d	7.6 (t, J_{cd} = 5.4 Hz, 1 H)
HO$\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}(CH_3)$=NNHAr	H_a	4.0 (t, J_{ab} = 5.4 Hz, 2 H)
	H_b	2.7 (t, J_{ab} = 5.4 Hz, 1 H)
	H_c	2.1 (s, 3 H)
$\overset{a}{C}H_3\overset{b}{C}H(OH)\overset{c}{C}(CH_3)$=NNHAr	H_a	1.4 (d, J_{ab} = 6.8 Hz, 3 H)
	H_b	4.5 (q, J_{ab} = 6.8 Hz, 1 H)
	H_c	2.1 (s, 3 H)
$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}(CH_2OH)$=NNHAr	H_a	1.0 (t, J_{ab} = 7.3 Hz, 3 H)
	H_b	2.4 (q, J_{ab} = 7.3 Hz, 2 H)
	H_c	4.4 (s, 2 H)

[a] In $CDCl_3$. [b] Internal $Si(CH_3)_4$ reference. [c] Ar = $C_6H_3(NO_2)_2$.

Experimental Section

Materials. The palladous chloride was purchased from Engelhardt, Inc. The nondeuteriated allylic alcohols (Aldrich Gold Label) were used as received. The crotyl alcohol-*1,1*-d_2 (**7'**) was prepared by reducing crotonyl chloride with $LiAlD_4$ following a literature procedure.[23] The methyl vinyl alcohol-2-d_1 (**10'**) was prepared by reducing methyl vinyl ketone with $LiAlD_4$ in anhydrous ether followed by treatment with aqueous NaOH solution. The alcohol was distilled using a microspinning band column. ^{1}H NMR indicated the isotopic purity of each was >98%. An authentic sample of 3-hydroxybutanal, **8**, was prepared from self condensation of acetaldehyde at 25 °C. All other chemicals were reagent grade.

Physical Measurements. All ^{1}H and ^{2}H NMR spectra were recorded on a Varian VXR-300 NMR spectrometer.

Product Identification and Analysis. With some slight modifications, the procedures were the same as those described previously for allyl alcohol oxidation.[3] In particular, when the 2,4-dinitrophenylhydrazone (2,4-DNP) derivative was prepared from authentic **8** at 25 °C, the ratio of **9**/**8** was 0.25. To prevent this dehydration the 2,4-DNP derivative was prepared at 2 °C. The reaction solution (25 mL) was 0.1 M in Li_2PdCl_4, 0.1 M in HCl, and 0.1 M in quinone (to prevent formation of π-allyl complexes). The substituted allyl alcohol (10% excess over Pd(II) present) was added gradually over a period of 20 min as opposed to 1–2 min for allyl alcohol itself. This was again to prevent formation of π-allylic complexes. The solution was stirred for

(23) Schuetz, R. D.; Millard, F. W. *J. Org. Chem.* **1959**, *24*, 297.

another 10 min, and the excess palladium(II) precipitated as Pd(0) by reaction with Zn powder. The reaction mixture was then cooled to ~2 °C. A (2,4-dinitrophenyl)hydrazine solution was prepared as previously described and also cooled to 2 °C. To this solution was added the cooled reaction mixture. The solids were collected and washed with water to remove any excess hydrazine reagent. After air drying the 2,4-DNP's were dissolved in hot benzene and filtered, and the extract was cooled to crystallize the 2,4-DNP's, which were then collected, dried, and dissolved in $CDCl_3$ for NMR analysis to determine total product distribution by ^1H NMR peak integration. Fortunately each product possessed a proton whose chemical shift was different from all other protons in the reaction mixture. For example in the oxidation of crotyl alcohol the crotonaldehyde vinylic protons at 6.3 ppm, the H_b protons of 8 at 4.2 ppm, the H_c protons of 13 at 4.6 ppm, and the H_a protons of 11 at 3.9 ppm were used for this purpose. The individual 2,4-DNP's of the products were separated by column chromatography as previously described.[3] The ^1H NMR spectra of the 2,4-DNP derivatives of the products are given in Table III. The products from the deuterium-labeling experiments were separated in the same fashion and analyzed by a combination of ^1H and ^2H NMR spectroscopy.

In order to obtain yields based on Pd(II) reduced, the reactions were run in the absence of quinone and the Pd(0) formed collected and weighed. The remaining Pd(II) was then precipitated with Zn dust, the reaction mixtures again filtered, and the filtrate analyzed for total carbonyls by an oximation procedure. The procedures for running the reactions and the carbonyl analysis by oximation have been described.[3] The yield values are an average of two determinations for each allyl alcohol. The variation between runs was less than 2%.

Kinetics Studies. The reactions were run in the presence of *p*-benzoquinone (Q), which oxidized the Pd(0) formed in the oxidation back to Pd(II). The benzoquinone is reduced to hydroquinone (QH_2) in the process. The extent of reaction was determined by measuring the emf of the cell: Pt/Q, QH_2, Pd(II), HCl, $LiClO_4$, olefin/Pd(II), HCl, $LiClO_4$, Q, QH_2/Pt. The apparatus and procedure has been described.[1]

The procedure for following the isomerization of 6′ or 7′ into its allylic isomer by ^2H NMR was the same as that used to follow the isomerization of deuteriated allyl alcohol.[8]

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A Simple Conversion of 1-Chloroethyl Carbonates to Fluoroformates: Value in the Preparation of Tertiary Alkyl Fluoroformates

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When the economical and easily available 1-chloroalkyl carbonates ($RCHClOCO_2R'$) are heated neat or in solution with KF in the presence of an 18-crown-6 catalyst, they fragment to aldehydes (RCHO) and fluoroformates (FCO_2R'). If the system is evacuated during reaction and either or both products are removed as formed, then the process is driven to completion and fluoroformates are isolated in good yield. The new methodology (*which exemplifies an unusual conversion of an ester to an acid halide*) is especially valuable in the synthesis of important tertiary alkyl fluoroformates and benzyl fluoroformate (with R as CH_3 in the carbonate): *tert*-butyl fluoroformate (Boc-F, 84% yield), *tert*-amyl fluoroformate (83%), 1-adamantyl fluoroformate (76%), benzyl fluoroformate (60%). Boc-F previously has been recommended as a superior reagent for the preparation of Boc-amino acids, but earlier routes to this reagent have been expensive and impractical. When R in the carbonate reactant is Cl_3C, the reaction proceeds cleanly without the 18-crown-6 catalyst (Boc-F in 79% yield). This latter variation is most useful on a small industrial scale.

In the preferred literature synthesis of most fluoroformates (FCO_2R), the analogous chloroformates ($ClCO_2R$) are simply stirred neat at or near room temperature with excess KF activated by a little 18-crown-6.[2,3] Fluoroformate yields normally are excellent (80–97%). However, this and other halide exchange processes[2] fail as routes to tertiary alkyl fluoroformates because the required precursor chloroformates are unstable; *tert*-butyl chloroformate decomposes to *tert*-butyl chloride at 0 °C.[4,5] Because attack at the benzylic carbon is preferred (to give benzyl fluoride), the method also fails as a source of benzyl fluoroformates. Both tertiary alkyl and benzyl fluoroformates can be made in good yield by acylating the respective alcohols with COF_2 or COFCl,[2] but the method is economically impractical due to the price of COF_2 ($700/lb, bp −83 °C) and the preparative inaccessibility of both COF_2 and COFCl in a standard laboratory.[6] In

(1) Both this paper and the following paper are dedicated by this author to the memory of his childhood friend and schoolmate through graduate school, Professor Emil Thomas Kaiser of Rockefeller University, deceased July 18, 1988.

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(6) For discussion, see footnote 5 in ref 2.

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