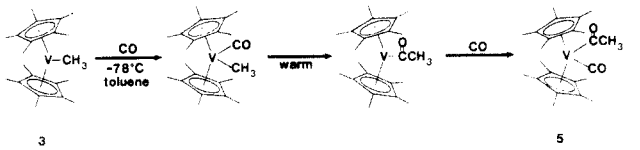

3 5

Figure 1. Reaction of methyl complex 3 with carbon monoxide.

assigned to the protons of the acetyl methyl group.

When complex **3** is treated with approximately 1 equiv of carbon monoxide at low temperature in an NMR tube, another diamagnetic complex is produced in addition to a small amount of **5**. This new complex also has a resonance in the proton NMR spectrum at δ 1.53 due to the ring methyl protons and a new peak at δ 0.26 which appears to be due to a methyl group on vanadium. When this sample is treated with more carbon monoxide, it is converted cleanly to **5**.

When complex **3** is titrated with carbon monoxide at room temperature and monitored by infrared spectroscopy, a slightly different result is obtained. After addition of 0.5 equiv of CO, the infrared spectrum shows a large absorption at 1596 cm^{-1} attributed to an acyl stretch and a very weak absorption at 1867 cm^{-1}. Addition of another 0.5 equiv aliquot of CO causes both of these bands to gain intensity. Addition of more CO increases the intensity of the band at 1867 cm^{-1}.

When this experiment is repeated and monitored by NMR, no signals are observed until 1 equiv of CO has been added and then only the signals due to acetyl carbonyl complex **5** are seen. These data can be reconciled as shown in Figure 1. Addition of CO to the methyl complex forms the methyl carbonyl complex which can be trapped and observed at low temperature. At room temperature, rapid CO insertion takes place to give an acetyl complex. This acetyl complex is paramagnetic, and so it is NMR silent and its acyl stretch occurs at 1596 cm^{-1}. Addition of more CO traps the acetyl complex as the diamagnetic acetyl carbonyl.

When the hydride complex **4** is exposed to carbon monoxide at 1 atm, a green, diamagnetic complex forms immediately. This complex is formulated as the simple carbonyl addition product bis(pentamethylcyclopentadienyl)vanadium carbonyl hydride **6**. The infrared spectrum of **6** shows a strong, terminal CO stretch at 1874 cm^{-1} and a medium-intensity metal–hydride stretch at 1681 cm^{-1}. The analogous complex prepared from **4**-d_1 and CO shows no absorption at 1681 cm^{-1} and a new band at 1221 cm^{-1}, confirming this assignment. The proton NMR spectrum shows a sharp resonance at δ 1.69 due to the ring methyl protons and a broad resonance at δ −7.34 due to the hydride ligand. The high-field chemical shift of this hydride resonance is in the same region as the hydride resonances of $Cp_2M(H)CO$ (M = Nb, δ −6.39; M = Ta, δ −6.80)[11] and is markedly different from the low-field shifts observed for the bis(pentamethylcyclopentadienyl)metal dihydrides of group 4[12] which reduce carbon monoxide.[4] No further reaction of **6** with CO is observed at pressures up to 25 atm.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Alcohol Fuels.

Registry No. 1, 74507-60-1; 2, 89710-27-0; 3, 96427-57-5; 4, 96427-58-6; 4-*d*, 96427-59-7; 5, 96427-60-0; 6, 96427-61-1; $(\eta^5$-$C_5Me_5)_2V(Me)CO$, 96427-62-2; $(\eta^5$-$C_5Me_5)_2V(COCH_3)$, 96427-63-3; CO, 630-08-0.

(11) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.

(12) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Oxidation of Olefins by Palladium(II). 10.[1] Products of the Reaction of $PdCl_4^{2-}$ with Allyl Alcohol in Aqueous Solution

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The reaction of allyl alcohol **7** with aqueous $PdCl_4^{2-}$ gave β-hydroxypropanal, hydroxyacetone, acrolein, propanal, propene, and traces of acetone as products. By deuterium isotope distribution studies using $CH_2{=}CHCD_2OH$ and $CD_2{=}CHCH_2OH$ as substrates, it could be shown that β-hydroxypropanal and hydroxyacetone were formed by the hydroxypalladation–hydride shift mechanism found for other acyclic olefins while acrolein was formed by a direct hydride extraction from the alcohol carbon. Propanal is formed in a secondary reaction by reduction of the acrolein while propene is formed by decomposition of intermediate (π-allyl)palladium(II) species. The acetone probably results from oxidation of the propene by $PdCl_4^{2-}$. The isotope effect, k_H/k_D, for hydride shift in the formation of β-hydroxypropanal is 1.9. This value is in close agreement with earlier results using ethene-*1,2*-d_2.

Introduction

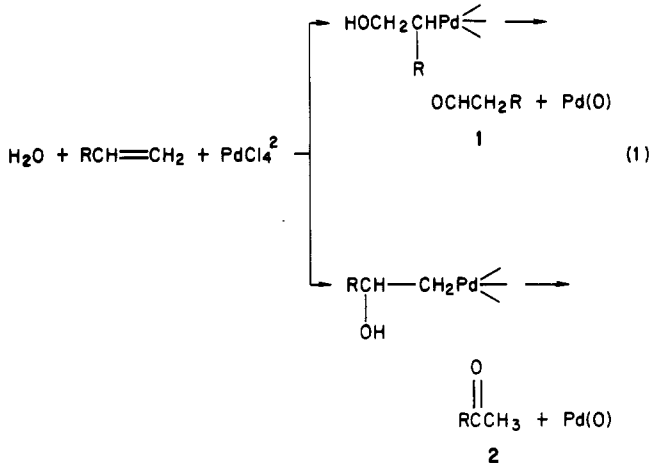
Allyl alcohol is a rather unique substrate in palladium(II) catalysis because both the olefin and alcohol functional groupings can participate in the reaction. It has been reported that allyl alcohol reacts with palladous chloride either without solvent or in 50% aqueous acetic acid solution to give, in addition to hydrofurfuryl alcohol derivatives obtained from addition of hydroxyl of one allyl alcohol to the double bond of another, propene, acrolein, propanal, and (π-allyl)palladium chloride plus other minor products.[3]

(1) Part 9: Winstein, S.; McCaskie, J.; Lee, H.-B.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 6913.

(2) Present Address: Loyola University of Chicago.

0276-7333/85/2304-1286$01.50/0

In aqueous acid solution acrolein is reported to be the organic product in 75% yield[4] with formation of some (π-allyl)palladium chloride.[5] This high yield of acrolein is somewhat surprising since, as shown in eq 1, α-olefins



usually give saturated aldehydes and ketones resulting from the two possible modes of hydroxypalladation.[6] For propene (R = CH_3) **1** is formed in 2–20% yield and **2** in 80–98% yield depending on reaction conditions.[7a] Jira has detected β-hydroxypropanal (**1**, R = CH_2OH) in the aqueous allyl alcohol reaction mixture and suggested that the acrolein arises from dehydration of this product as shown in eq 2.[7b] However, previous studies have indicated

$$HOCH_2CH_2CHO \xrightarrow{-H_2O} CH_2{=}CHCHO \qquad (2)$$

that under the reaction conditions the dehydration is very slow and the equilibrium is 90% on the side of β-hydroxypropanal.[8]

Because of this uncertainty, this study of the product distribution resulting from the oxidation of allyl alcohol in aqueous solution was undertaken. In addition the mechanism of formation of each product was determined by deuterium-labeling experiments. Preliminary reports of parts of this work have appeared.[9,10]

Results

Product Distribution. All reactions were carried out at 25 °C. A combination of GLC analysis, gas uptake measurements, ^1H and ^2H NMR spectra, Fehling's solution titration, an oximation procedure, and (2,4-dinitrophenyl)hydrazone derivative preparation followed by column chromatography were used to identify the products and determine their yields. A serious complication was the fact that the β-hydroxypropanal existed mainly as a dimer in aqueous solution.[8] The product distribution based on Pd(0) formed under one set of reaction conditions is shown in eq 3.

$$\underset{7\ (0.3\ M)}{CH_2{=}CHCH_2OH} \xrightarrow[[Cl^-] = 0.2\ M]{[PdCl_4^{2-}] = 0.2\ M,\ [H^+] = 0.2M} \underset{1\ (40\%,\ \text{mainly dimers})}{HOCH_2CH_2CHO} + \underset{2\ (12\text{–}15\%)}{CH_3C(=O)CH_2OH} + \underset{3\ (30\%)}{CH_2{=}CHCHO} + \underset{4\ (2\%)}{CH_3C(=O)CH_3} + \underset{5\ (15\%)}{CH_3CH_2CHO} + \underset{6\ (7\%)}{CH_2{=}CHCH_3} \qquad (3)$$

The last three products, are, of course, not oxidation products so total yields of oxidation products are over 80%. Since the finding of both the usual saturated products (β-hydroxypropanal (**1**) and hydroxyacetone or acetol (**2**)) as well as acrolein (**3**), it was of interest to see if all were formed by the same rate expression. To do this would require product distribution determinations at several different $[PdCl_4^{2-}]$, $[Cl^-]$, and $[H^+]$. As this would be extremely tedious, an alternate procedure was used. The reactions were runs in D_2O, and the acetol to acrolein ratios were determined by ^1H NMR. This is an approximate procedure since the ratios of acetol and β-hydroxypropanol can vary in the same way acetone to propanal ratios vary in propene oxidation.[7a] Results are given in Table I. There is some variation but not enough to suggest a different rate expression. Thus the change from 29% acetol to 38% acetol in going from $[Cl^-] = 0.1$ to $[Cl^-] = 1.0$ M is small compared to that expected for different kinetic chloride dependences. The biggest variations are in runs 4–6 but again not large enough to have different proton terms in the rate expression.

The presence of propanal and acetone could have arisen from oxidation of the propene formed but, as discussed in the Introduction, acetone would have been expected to be the major product. To determine factors the propanal/acetone ratio was determined at two different reaction times. At 20 min, the propanal/acetone ratio was 12 while at 120 min, it was 2, indicating that acetone is formed by secondary oxidation of propene while propanal is not. Deuterium-labeling experiments to be described below confirm this assumption.

Deuterium-Labeling Studies. These studies will be discussed in terms of the reaction products.

(1) The β-hydroxypropanal product mixture was the same from the oxidation of either $CH_2{=}CHCD_2OH$ (**7a**) or $CD_2{=}CHCH_2OH$ (**7b**). This product mixture consisted of $HOCD_2CH_2CHO$ (**1a**) and $HOCH_2CHDCDO$ (**1b**) in a ratio **1a**/**1b** of 1.9.

(2) The hydroxyacetone product from **7a** was almost exclusively $CH_3C(O)CD_2OH$ (**2a**) while that from **7b** was $CD_2HC(O)CH_2OH$ (**2b**).

(3) The acrolein product from **7a** was 96% $CH_2{=}CHCDO$ (**3a**) and 4% $CD_2{=}CHCHO$ (**3b**) while that from **7b** was 96% **3b** and 4% **3a**. The amount of the other isomer in each case can be explained by the Pd(II)-catalyzed isomerization of the starting deuterated allyl alcohol during the course of the oxidation.[11]

The isotope effect for acrolein formation was determined by a competitive experiment using equal concentrations of nondeuterated allyl alcohol and **7a**. The isotope effect k_H/k_D, which is equal to $CH_2{=}CHCHO$/**3a**, was found to

(3) (a) Smidt, J.; Hafner, W. *Angew Chem.* **1959**, *71*, 284. (b) Urry, W. H.; Sullivan, M. B. *Prepr.—Am. Chem. Soc. Div. Pet. Chem.* **1969**, *14* (2), B131. (c) Hafner, W.; Pregge, H.; Smidt, J. *Justus Liebigs Ann. Chem.* **1966**, 693, 109.

(4) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176. (b) Smidt, J.; Sieber, R. *Ibid.* **1959**, *71*, 626.

(5) (a) Moiseev, I. I.; Fedorovskaya, E. A.; Syrkin, Y. K. *Russ. J. Inorg. Chem. (Eng. Transl.)* **1959**, *4*, 1218. (b) Pietropaolo, R.; Uguagliati, P.; Boschi, T.; Crociani, B.; Belluco, U. *J. Catal.* **1970**, *18*, 338.

(6) For general discussion and references see: Henry, P. M. Palladium Catalyzed Oxidation of Hydrocarbons"; D. Reidel: Dordrecht, Holland, 1980. After this book was completed, a report of a kinetic study of the oxidation of allyl alcohol by palladium(II) chloride in aqueous *basic* solution appeared in which potassium hexacyanoferrate(III) was used as a reoxidant for Pd(0) (Ahmed, I.; Ashraf, C. M. *Int. J. Chem. Kinet.* **1979**, *11*, 813). In this paper acetol was reported as a product. However, no yields were given.

(7) (a) Hafner, W.; Jira, R.; Sedlmeier, J.; Smidt, J. *Chem. Ber.* **1962**, *95*, 1575. (b) Jira, R. *Tetrahedron Lett.* **1971**, 1225.

(8) Hall, R. H.; Stern, E. S. *J. Chem. Soc.* **1950**, 490.

(9) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.

(10) Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1983**, *2*, 197.

(11) Gregor, N.; Zaw, K.; Henry, P. M. *Organometallics* **1984**, *3*, 1251.

be 1.8 ± 0.1 (average of six runs).

(4) The propanal products from **7a** were CH_3CH_2CDO (**5a**) and CH_2DCH_2CDO (**5a'**), and the propanal product from **7b** was CD_2HCH_2CHO (**5b**). The ratio of **5a**/**5a'** was 3/2. No deuterium lines from deuterated acetone were detected in the ^2H NMR spectra of the carbonyl products.

Nondeuterated allyl alcohol was oxidized in D_2O containing DCl and the deuterium distribution of the propanal product studied by ^1H and ^2H NMR and mass spectra. The expected products were CH_3CH_2CHO (**5**), CH_2DCH_2CHO (**5c**), $CH_3CHDCHO$ (**5d**), and $CH_2DCHDCHO$ (**5e**). NMR could not differentiate the various possibilities so the mass spectra of the (2,4-dinitrophenyl)hydrazones were used to measure the ratios. The mixture consisted of 58% **5** while **5c** plus **5d** totaled 23% and **5e** was the remaining 19%.

(5) The propene product from *both* **7a** and **7b** consisted of a 50:50 mixture of $CH_3CH{=}CD_2$ (**6a**) and $CD_2HCH{=}CH_2$ (**6b**).

Discussion

Hydroxycarbonyl Products. One noteworthy result of this study is the demonstration that allyl alcohol gives the products β-hydroxypropanal and acetol expected on the basis of the oxidation of other acyclic olefins (see eq 1). Also the products from the two deuterated allyl alcohols **7a** and **7b** were those expected from eq 1. Thus, as shown in eq 4, **7a** gives **8a** by Markovnikov hydroxypalladation.

$$2H_2O + \mathbf{7a} + PdCl_4^{2-} \xrightarrow[-H^+]{-2Cl^-} {}^-(H_2O)Cl_2PdCH_2C(OH)HCD_2OH \rightarrow \underset{\mathbf{8a}}{} CH_3C(=O)CD_2OH + Pd(0) + 2Cl^- + H_2O \quad (4)$$
2a

The situation with non-Markovnikov addition is of special interest because, as shown in eq 5, if **7a** and **7b** give the same hydroxypalladation adduct, they would be expected to give the same distribution of deuterated isomers **1a** and **1b**. As shown in eq 5 they do, in fact, give the same product distribution. Of course this is very good evidence for the generally accepted hydroxypalladation mechanism.

$$2H_2O + \mathbf{7a}\text{ or }\mathbf{7b} + PdCl_4^{2-} \xrightarrow[-H^+]{-2Cl^-} HOCH_2CHCD_2OH \longrightarrow \underset{\mathbf{9}}{PdCl_2(H_2O)^-}$$

$$HOCD_2CH_2CHO + HOCH_2CHDCDO + Pd(0) + 2Cl^- + H_2O \quad (5)$$
1a (1.9) **1b** (1.0)

Since formation of **1a** requires a hydride shift[12] and formation of **1b** requires a deuteride shift, the ratio of **1a**/**1b** is a measure of the isotope effect k_H/k_D. The value of 1.9 is close to the value of 1.8 (1.7,[13] 1.86[14]) found previously for the oxidation of 1,2-ethene-d_2.

Mention should be made of the fact that the aldehyde product β-hydroxypropanal is found in considerable greater yield than the ketone product acetol while with most α-olefins, the ketone is the predominant product. However, olefins with electron-withdrawing substituents give mainly the aldehyde product.[5b,7a]

Acrolein Formation. Probably the most novel result of this study is the demonstration that acrolein is *not* formed by dehydration of β-hydroxypropanal but rather by direct hydrogen or deuterium extraction from the alcohol carbon. Thus the fact **7a** gives almost exclusively **3a** and **7b** almost exclusively **3b** is completely inconsistent with their formation by dehydration of the mixture of **1a** and **1b** in eq 5, for if that were the case both **7a** and **7b** would give the same mixture of **3a** and **3b**.

Table I. Ratios of Acetol to Acrolein in D_2O under Various Reaction Conditions[a]

$[D^+]$, M	$[Cl^-]$, M	acetol, %	acrolein, %
0.1	0.1	29	71
0.1	0.2	33	67
0.1	0.5	32	68
0.1	1.0	38	62
0.6	0.6	43	57
1.0	1.2	66	33

[a] $[PdCl_4^{2-}]$ = 0.2M for all runs, 25 °C.

The oxidation of allyl alcohol directly to acrolein is of itself not surprising since the oxidation of saturated alcohols by palladium(II) salts to aldehydes and ketones was discovered by Berzelius[15] over 150 years ago and since then has been studied by several workers.[16-20] Recently, the kinetics of oxidation of methanol, ethanol, and 2-propanol by palladium(II) chloride has been studied in the temperature range 66–76 °C.[21]

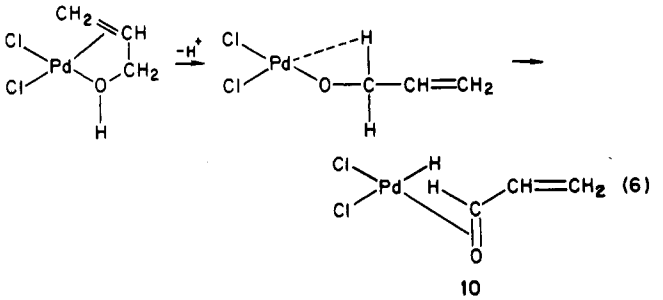
As suggested by previous workers[21-23] the mechanism almost certainly involves a hydrogen extraction from the alcoholic carbon by Pd(II) to give Pd(II) hydride and in analogous reactions of alcohols with Pt(II), Ru(II), and Ir(III) stable hydrides have been isolated.[24] The one feature that distinguished allyl alcohol oxidation from saturated alcohol oxidation is the much faster rates for the former. Thus, rate of acrolein formation at 25 °C is much faster than rates of acetone formation from 2-propanol at 96 °C reported in the study mentioned previously.[21] The faster rates for allyl alcohol oxidation must reflect olefin coordination which facilitates hydride abstraction by holding alcohol in close proximity to the Pd(II).

The data in Table I show some variation in acetol/acrolein ratios but they are probably not sufficiently large to be caused by different chloride or proton dependencies in the rate expressions. Certainly in the cases of chloride concentration this is true since there is little variation in the ratio while $[Cl^-]$ is changed by a factor of 10 (runs 1–4). On the other hand, there is a larger variation in runs 4–6 where $[H^+]$ is varied by a factor of 10 and a much larger change in ratio would have been expected if there were a real difference in proton dependence. It is noteworthy that the acetol/acrolein ratios in D_2O in Table I are about the same as in H_2O (see eq 3). This is surprising in light of the fact that the solvent isotope effect, k_{H_2O}/k_{D_2O}, for oxidation of ethylene is 4.05[25] and the same solvent isotope effect for oxidation of isopropanol to acetone was found

(12) For a discussion of the mechanism of the hydride shift see ref 6, pp 76–78.
(13) Henry, P. M. *J. Org. Chem.* **1973**, *38*, 2415.
(14) Kosaki, M.; Isemura, M.; Kitaura, Y.; Shinoda, S.; Saito, Y. *J. Mol. Catal.* **1977**, *2*, 351.
(15) Berzelius, J. J. *Justus Liebigs Ann. Chem.* **1828**, *B13*, 435.
(16) Lloyd, W. G. *J. Org. Chem.* **1967**, *32*, 2816.
(17) Ketley, A. D.; Fisher, L. P. *J. Organomet. Chem.* **1968**, *13*, 243.
(18) Nikiforova, A. V.; Moiseev, I. I.; Syrkin, Y. K. *Zh. Obshch. Khim.* **1963**, *33*, 3239.
(19) Brown, R. G.; Davidson, J. M.; Triggs, C. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1969**, *14* (2), B23.
(20) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157.
(21) Kozkevnikov, I. V.; Taraban'ko ko, V. E.; Matveev, K. I. *Kinet. Katal.* **1980**, *21*, 940; *Kinet. Catal. (Engl. Transl.)* **1980**, 679.
(22) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. II, p 119.
(23) Stern, E. V. *Usp. Khim.* **1973**, *42*, 232.
(24) Dobson, A.; Robinson, S. D. *J. Organomet. Chem.* **1975**, *87*, 52.
(25) Moiseev, I. I.; Vargaftik, M. N.; Sirkin, Y. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 1144.

to be 1.3.[21] It is a unique result indeed for two quite different reactions to have the same rate expression as well as solvent isotope effects.

Since the rate expression for oxidation of acyclic olefins to aldehydes and ketones has a square chloride inhibition and a first power proton inhibition,[5] the acrolein formation would be expected to have analogous inhibition terms. A general reaction sequence consistent with such a rate expression is shown in eq 6. The uncomplexing of the olefins

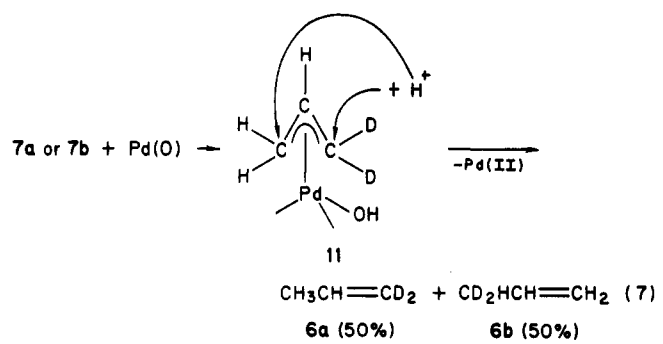


(6)

10

is postulated to provide a vacant coordination site for hydride elimination.[26] The isotope effect k_H/k_D of 1.8 for the oxidation of allyl alcohol is identical with that measured for a similar competitive experiment[21] using *i*-C_3D_7OD and *i*-C_3H_7OH, indicating that the two hydride eliminations are similar processes. It is interesting that this isotope effect is close to that found for the breaking of a C–H bond in the decomposition of the intermediate **9** (eq 5).

Propene Formation. The fact that both **7a** and **7b** gave a 50:50 mixture of the two possible deuterated propenes **6a** and **6b** is strong evidence for a symmetrical π-allyl intermediate. One possible reaction scheme is shown in eq 7.

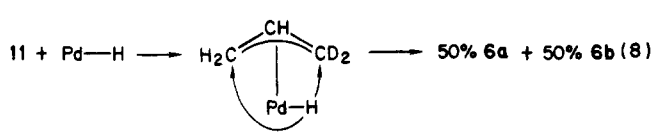


11

$CH_3CH{=}CD_2$ + $CD_2HCH{=}CH_2$ (7)

6a (50%) **6b** (50%)

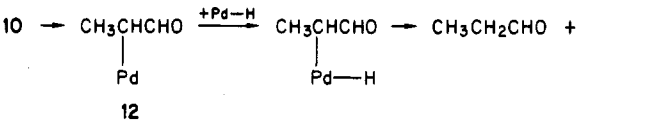
The propene formation tends to regenerate Pd(II) from Pd(0) so actually the yields in eq 3 based on weights of final palladium metal precipitate are a little high since some Pd(0) was removed by the reaction in eq 7. The proton attack on 11 in eq 7 may be oversimplified. Hydride species may be involved as shown in eq 8. However,



since π-allyl species can be formed by proton exctraction from propene by base in the presence of Pd(II),[27,28] by the principle of microscopic reversibility, the reverse reaction would be expected to take place. It is also very likely that the π-allylic species protonated to give propene is not the stable chloride-bridged dimeric species. In any case both modes of decomposition of π-allyls have been suggested in the mechanism for reactions of 1,3 dienes.[29a]

At this point a few words on previous studies of decomposition of π-allyls in aqueous solution are appropriate.[29b] In the presence of oxidants allylic carbonyl compounds are products. As discussed previously this route for formation of acrolein is completely eliminated by the deuterium isotope labeling studies. In the absence of added oxidant (π-allyl)palladium chloride gives an equimolar mixture of acrolein and propene or allyl alcohol and propene depending on acidity of the media. Certainly the present work does little to clarify the mechanisms of these processes, but it would be interesting to prepare the stable form of 11 and decompose it in aqueous solution. Both the allyl alcohol as well as the acrolein would be expected to show deuterium-labeling patterns characteristic of a symmetrical intermediate.

Propanal and Acetone Formation. The formation of propanal was not predicted, but its presence is not too surprising since a very natural reaction for the hydride species **10** in eq 6 is to add the hydride across the double bond to give the alkyl **12** as shown in eq 9.



12

Pd(0) (9)

Another Pd(II) hydride can transfer hydride to **12** followed by reductive elimination of Pd(0) to complete the reduction as shown. Of course the second hydride species would have been formed by the oxidation of another allyl alcohol to acrolein. All that is required is that the propanal yield be equal to or less than the acrolein yield since one extra hydride is need for propanal formation. This is certainly the case as shown in eq 3.[30]

The postulated intramolecular and intermolecular hydride-transfer schemes in eq 6 and 9 are strongly supported by the deuterium-labeling studies. The fact that **7a** gives only RCDO and **7b** gives only RCHO indicates the hydrogen was initially extracted from the alcohol carbon as shown in eq 6. The fact that reaction of nondeuterated allyl alcohol in D_2O gives over half nondeuterated propanal product indicates most of the hydrogen comes from hydride extraction from the alcohol carbon of the starting alcohol. The fact that the remaining propanal contains one to two deuterium indicates that these can be hydride exchange with solvent before both intra- or intermolecular hydride participation in the reduction of the double bond. It could be simple exchange or reductive elimination–oxidative addition type mechanism.[31] It appears that the deuteride species formed in the reaction of **7a** exchanged to greater extent with H_2O than the hydride species from ordinary allyl alcohol exchanged with D_2O. Thus, only 40% of the product is CH_2DCH_2CDO while no $CH_2DCHDCDO$ was detected. This result must reflect the isotope effects for the exchange processes.

There is considerable analogy for the hydrogen shift mechanism in transition-metal chemistry. Thus ruthe-

(26) The detailed reaction paths for hydroxycarbonyl products and acrolein will be discussed in a full paper on the kinetics and mechanisms of these processes. Equation 6 was suggested by a reviewer.

(27) Morelli, D.; Ugo, R.; Conti, F.; Donati, M. *J. Chem. Soc., Chem. Commun.* **1967**, 801.

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(29) (a) Reference 6, pp 256–260. (b) Reference 6, pp 275–277.

(30) It is interesting to note that propanal *plus* propene yields add up to the acrolein yield. Thus some of the hydride formed in acrolein production could have been used for propanal formation and some for propene formation.

(31) For a discussion of the reactions of Pd(II) hydrides see ref 22, Vol. I, pp 103–105.

Table II. ^{1}H NMR (400-MHz) of (2,4-Dinitrophenyl)hydrazone Derivatives of Carbonyl Products[a]

derivative	proton	chemical shifts,[b] ppm
(a) (b) (c) $CH_3CH_2CH{=}NNHC_6H_3(NO_2)_2$	H_a	1.2 (t, J_{ab} = 6.3 Hz, 3 H)
	H_b	2.4 (m, J_{bc} = 5.3 Hz, 2 H)
	H_c	7.4 (t, 1 H)
(a) (c) H H \ / C=C / \ H C=NNHC$_6$H$_3$(NO$_2$)$_2$ H (d)	H_a	5.7 (m, J_{ab} = 2.2 Hz, J_{ac} = 10.3 Hz)
	H_b	5.7 (m, J_{bc} = 16.9 Hz)
	H_c	6.6 (m, J_{cd} = 8.8 Hz, 1 H)
	H_d	7.8 (d, 1 H)
(a) (b) (c) $HOCH_2CH_2CH{=}NNHC_6H_3(NO_2)_2$	H_a	4.0 (t, J_{ab} = 5.8 Hz, 2 H)
	H_b	2.8 (td, J_{bc} = 5.1 Hz, 2 H)
	H_c	7.6 (t, 1 H)
(a) (b) $HOCH_2C(=NNHC_6H_3(NO_2)_2)CH_3$	H_a	4.4 (s, 2 H)
	H_b	2.1 (s, 3 H)

[a] In $CDCl_3$. [b] Internal $Si(CH_3)_4$ reference.

nium(II) catalyzes the conversion of allyl alcohol to propanal, propene, and acrolein in 50% aqueous alcohol,[32] and hydrogenation of olefins with palladium(II) complexes can be carried out by using alcohols as a source of hydrogen.[33] Chloromethyl methyl sulfoxide complexes of palladium and rhodium are reported to give propanal from allyl alcohol in the presence of H_2, but the palladium catalyst is inactive in the absence of H_2 while the rhodium catalyst retains its activity.[34] The mechanism of these reactions must also involve hydride elimination and readditions. Similar mechanisms are also no doubt operative in the hydrogen transfer from alcohols to ketones.[35]

The acetone is a minor product, and since it would have been a tedious procedure to isolate such a minor product and determine its deuterium distribution, no attempt was made to do so.[36] In any case it is difficult to imagine any route for its formation other than the oxidation of propene by palladium(II) salts. The fact that the propanal/acetone ratio decreases at longer reaction times is further evidence that acetone is formed in a secondary oxidation.

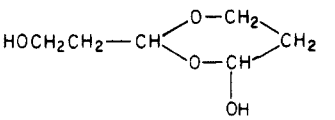
Experimental Section

Materials. The palladous chloride was purchased from Engelhardt, Inc. The nondeuterated allyl alcohol, acrolein, acetol, and propanal (all Aldrich Gold Label) were used as received. The allyl-*1,1*-d_2[37] and -3,3-d_2[38] alcohols were prepared by literature procedures. ^{1}H NMR indicated the isotopic purity of each was >98%. All other chemicals were reagent grade.

Physical Measurements. All proton and deuterium NMR spectra were recorded on a Brucker 400-MHz and Varian 80-MHz NMR spectrometers. Mass spectra were recorded on the Hewlett-Packard 5985 GC/MS system of Northwestern University, Evanston, IL. GLC analyses were carried out on a Hewlett-Packard research chromatograph (Model HP 5750 B).

General Procedure. The reaction solution was 0.2 M in Li_2PdCl_4 and 0.2 M in HCl. The new reactions were usually run on a 25–50 mL scale. With stirring an amount of allyl alcohol about 10% in excess of the Pd(II) present was added over a period of 1–2 min. The stirring was continued for another 10–20 min. The reaction mixture was filtered carefully to completely remove all Pd(0) precipitate; the precipitate was washed with water and ethanol, dried, and weighed. All yields are based on the moles of Pd(0) formed. The remainder of the Pd(II) was then removed by the careful addition of zinc dust. The solution was then filtered again and the filtrate used for product determination. Most reactions were run in open flasks although several were in closed systems which were connected to a gas buret in order to detect and measure the quantities of any gaseous products formed.

Preliminary ^{1}H NMR Identification of Products in D_2O. The reaction was run on a 10-mL scale using DCl in place of HCl. After removal of palladium, the ^{1}H NMR spectrum was run and compared with spectra of authentic samples of possible products run in D_2O. The determination was complicated by the fact that pure β-hydroxypropanal cannot be obtained since it dimerizes spontaneously.[8] In aqueous solution it is reported to exist mainly as the dimer **13**.[8] In order to prepare standards, acrolein was



13

hydrated in D_2O catalyzed by DCl. The ^{1}H NMR gave resonances clearly assignable to β-hydroxypropanal. In addition where was a set of broad resonances (0.5–3.5 ppm) which can be attributed to the dimeric species **13**.

Integration of the spectrum of the original reaction mixture gave the following relative yields: acrolein, 32%, acetol, 16%; propanal, 9%; β-hydroxypropanal as monomer and dimer, 38% (11% as a monomer); other carbonyl products, 5%.

Isolation as (2,4-Dinitrophenyl)hydrazone Derivative by Column Chromatography. For this analysis the reaction was run on a 50-mL scale. A (2,4-dinitrophenyl)hydrazine solution was prepared by dissolving 3.0 g of the reagent in 15 mL of concentrated H_2SO_4 at room temperature. This solution was carefully added to 80 mL of water, and the mixture stirred for 10 min and filtered. To 50 mL of this clear orange solution cooled to ca. 5 °C was added, with stirring, the reaction mixture in 10-mL portions. After the mixture was stirred for 10 min at 10–15 °C, the bright orange precipitate was filtered, washed several times with distilled water, and dried in a cold stream of air.

For the chromatographic separation a column 2.5 cm in diameter was packed to a depth of 17 cm with alumina. About 0.75 g of the derivative was dissolved in 25–30 mL of benzene and charged on the column. The first fraction eluted with benzene was a mixture of the acrolein and propanal derivatives which could not be separated by this technique. The second fraction, eluted with benzene/ethyl acetate (20:1 by volume), contained the acetol

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(36) The propene formed is a mixture of **6a** and **6b**. Oxidation of either by Markkovnikov hydroxypalladation followed by hydride shift would give $CD_2HC(O)CH_3$ (**4a**) from either **6a** or **6b** so **4a** would have expected if acetone was a secondary product of propene. Other routes might give different deuterated isomers.
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derivative. The third fraction, eluted with benzene/ethyl acetate (5:1 by volume), was the β-hydroxypropanal derivative.

In control experiments samples of acrolein were hydrated to mixtures of β-hydroxypropanal and the dimer **13**. The (2,4-dinitrophenyl)hydrazone derivative was prepared and chromatographed. Recovery of the β-hydroxypropanal derivative was 10–15% based on acrolein. The ^1H NMR spectra of the derivatives carbonyl of the products are given in Table II.

GLC Analysis. Several analyses for volatile products were carried out on neutralized reaction mixtures using a 6 ft. 20% Carbowax 20 M column on 60–80 mesh Chromosorb W. The column was programmed from 70–200 °C at 10 °C/min. Propanal and acrolein were not resolved by this procedure but by the use of standards it could be calculated this combined yield was 45–50%. Acetol could be identified and analyzed by the use of standard solutions. Its yield was 12–15%.

Chemical Analysis. As the dimer of β-hydroxypropanal is reported[8] to be depolymerized by oximation, total carbonyl products were determined by this method using a literature procedure.[39,40] The reaction was run on a 50-mL scale and, after removal of palladium, was diluted to 100 mL (A). A 10-mL portion of A was treated with 50 mL of freshly prepared 0.1 M hydroxylamine hydrochloride at 45 °C for 30 min, cooled, and potentiometrically titrated with 0.1 M NaOH (V_1). Another 10-mL portion of A was also titrated with the base (V_2). The difference $V_1 - V_2$ was a measure of the total carbonyl products.

A 50-mL portion of A was extracted several times with ether to remove acetone, acrolein, propanal, and unreacted alcohol. The residue ether was removed from A under vaccuum to give B which contained mono and dimeric β-hydroxypropanal and acetol. A 10-mL portion of B was oximated as described above and titrated potentiometrically with 0.1 M NaOH. The difference $V_1 - V_3$ was a measure of acetone, acrolein, and propanal while $V_3 - V_2$ was a measure of acetol and β-hydroxypropanal.

Acetol was determined by Fehling's solution which reacts rapidly with acetol even in the cold.[41,42] A 10-mL portion was reacted at 5 °C for 3–5 min, and the amount of Cu_2O was determined quantitatively in an inert atmosphere. From $V_3 - V_2$ and the acetal determination the amount of β-hydroxypropanal can be calculated.

In summary this analysis gave the following results: acetone plus acrolein plus propanal, 47%; acetol, 15%; β-hydroxypropanal, 38%.

Propene Analysis. As mentioned previously some runs were carried out in closed systems connected to gas burets to detect and measure any gaseous products such as propene. It was found that, in fact, a gas was given off which corresponded on a mole basis to about 7% of the Pd(0) formed. The gas was passed into a solution of Br_2 in CS_2. After the Br_2 color had disappeared, the solution was evaporated and the ^1H NMR of the solution taken in $CDCl_3$. The material was clearly 1,2-dibromopropane, indicating the gaseous product was propene: ^1H NMR CH_3, δ 1.85 (d, 3 H); CHBr, δ 4.18 (m, 1 H), CH_2Br, δ 3.80–3.49 (m, 2 H).

Deuterium-Labeling Experiments. The reactions were run in the same fashion as for the nondeuterated but on never more than a 25-mL scale. (2,4-Dinitrophenyl)hydrazone derivatives were prepared and chromatographed as previously described. The propene was also collected and converted to the dibromide derivatives. A combination of the ^1H and ^2H 400-MHz spectra readily permitted positive identification of all deuterated isomers as well as their relative amounts.

The propanal from the experiments in D_2O were converted to the (2,4-dinitrophenyl)hydrazone derivatives and the deuterium content analyzed by GC/MS.

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Registry No. D_2, 7782-39-0; $LiPdCl_4$, 15525-45-8; $CH_3CH_2CH{=}NNHC_6H_3(NO_2)_2$, 725-00-8; $CH_2{=}CHC{=}NNHC_6H_3(NO_2)_2$, 888-54-0; $HOCH_2CH_2CH{=}NNHC_6H_3(NO_2)_2$, 40365-04-6; $HOCH_2C(=NNHC_6H_3(NO_2)_2)CH_3$, 96481-90-2; allyl alcohol, 107-18-6.

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Relative Acidifying Effects of Tricarbonylchromium(0) and *p*-Nitro Groups upon Di- and Triphenylmethanes

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The kinetic and thermodynamic acidities of the tricarbonylchromium(0) or *p*-nitro-substituted di- and triphenylmethanes **1–6** have been measured in methanol–dimethyl sulfoxide solutions. The kinetic acidifying influence of a single tricarbonylchromium(0) group is found to be greater than that of a single *p*-nitro substituent in these molecules, but the acidifying effect of the tricarbonylchromium(0) group is not cumulative and steric effects become increasingly evident in these complexed molecules. The thermodynamic acidities of the nitro-substituted aromatics are greater than those of their tricarbonylchromium(0)-complexed analogues, in accord with the greater charge delocalization in their carbanions by the nitro group.

Introduction

There have been several studies reported on the generation[1-4] and structures[4-9] of aryl or arylmethyl carbanions stabilized by complexation with one or more tricarbonylchromium(0) groups. It has been demonstrated

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