Hydration of Diethyl Maleate in the Presence of Bimetallic Hydroxy Palladium(II) Complexes of 1,2-Bis(diphenylphosphino)ethane(dppe) as Catalysts

Sanjoy Ganguly and D. Max Roundhill*
Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA

The hydration of diethyl maleate is catalysed by the presence of [Pd(μ-OH)(dppe)]$_2$(BF$_4$)$_2$ in solution.

The hydration of alkenes is a potentially important route for the synthesis of alcohols. The reaction requires a catalyst, and ones which are used include sulphuric acid, phosphoric acid[1] or proton-exchanged zeolites.[2,3] For fluoroethylenes, solutions containing chlororuthenate(II) species have been used as homogeneous catalysts.[4] Even though the catalysed hydration of both fumaric and maleic acid can be effected by fumarase and chromium(III) chloride respectively,[5,6] very few compounds catalyse the hydration of alkenes.[7] We now report that the hydration of diethyl maleate to diethyl malate is catalysed by solutions of [Pd(μ-OH)(dppe)]$_2$(BF$_4$)$_2$,[8] albeit with a very small turnover number of 14.

Scheme 1

$\overparen{P \quad P}$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
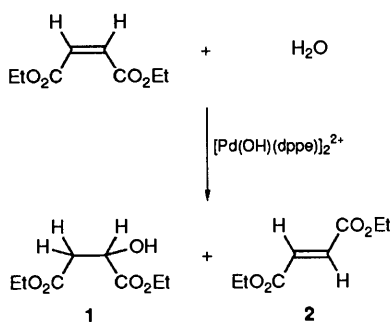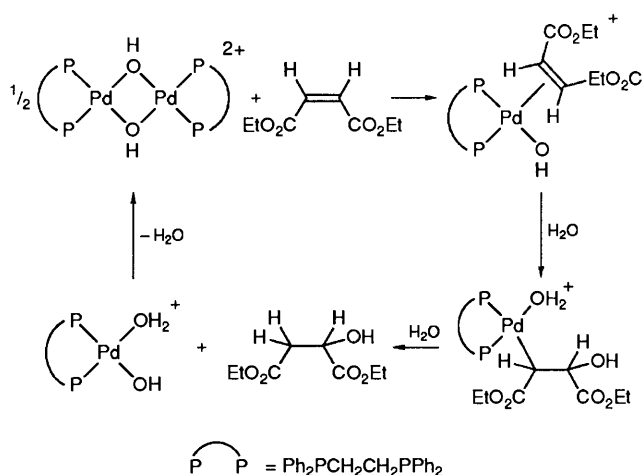
Scheme 2

When a solution containing diethyl maleate (190 mol), [Pd(μ-OH)(dppe)]$_2$(BF$_4$)$_2$ (1 mol), and water (3415 mol) is heated for 30 h at 140 °C in a sealed glass tube, both diethyl malate **1** (14.1 mol) and diethyl fumarate **2** (17.3 mol) are formed (Scheme 1). These products are identified by GC–mass spectral comparison with authentic samples. The yields are measured by integration of the baseline resolved peaks in the GC–mass spectrum after correcting for the relative instrument sensitivity to the compounds. The results are reproducible. The other products of the reaction are maleic acid or its anhydride (24 mol). When the reaction is carried out in D$_2$O we observe, by GC–mass spectral analysis, the formation of the deuteriated derivative of diethyl malate. After 30 h, the metal complex has completely decomposed to palladium metal. The reduction to palladium metal occurs because of the formation of the reductant, ethyl alcohol, in the hydrolysis of diethyl maleate. No increase in the yield of diethyl malate is observed if the reaction time is extended to 60 h from 30 h. No decrease in yield is found when elemental mercury is added to the reaction solution. The addition of sodium hydroxide (pH 8 or 12) or phosphoric acid (pH 2, 3, 4 or 5) suppresses the formation of diethyl malate. The addition of copper(II) to the reaction reduces the yield of malic ester to 2 mol. The addition of 1 equiv. of dppe to the solution causes no increase in the yield of malic ester, but the addition of 6 equiv. of dppe decreases the yield by more than seven-fold. This decrease corresponds with a 100-fold increase in the yield of diethyl fumarate. Neither the *trans*-isomer, diethyl fuma-
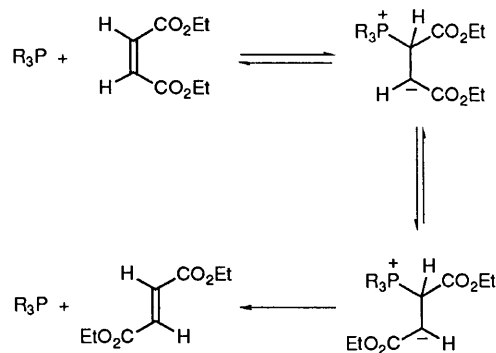
Scheme 3

rate, nor the free maleic acid undergo hydration in the reaction. We observe no formation of succinic acid or tartaric acid.

The 60 h reaction time results, along with the observed failure of elemental mercury to inactivate the catalyst, suggests that palladium metal is not the active catalyst.[9] The suppression of the conversion to malic ester by hydroxide ion, and the inhibition of the hydration of diethyl maleate by copper(II) ion, argues against a Wacker type mechanism.[10] Such a mechanism involves attack by hydroxide ion or water at a complexed alkene. The suggested pathway shown in Scheme 2 explains our results. The failure to observe hydration of diethyl fumarate is to be expected since the coordination of the *trans*-isomer will be sterically less favoured than the *cis*.

The isomerization of diethyl maleate to diethyl fumarate with added dppe occurs even in the absence of the palladium complex. In addition to dppe, we find that the addition of PPh$_3$, PMePh$_2$ or P(cyclohexyl)$_3$ to diethyl maleate gives diethyl fumarate in yields of over 80% after 30 h at 120 °C. This result appears to differ from that in recently published work.[11] The difference is likely due to our use of water as a solvent rather than the less polar toluene. A plausible pathway for this isomerization is shown in Scheme 3.

We thank the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for support of this research.

References

1 P. Wiseman, *An Introduction to Industrial Organic Chemistry*, Applied Science, London, 1979.
2 K. Eguchi, T. Tokiai and Y. Kimura, H. Arai, *Chem. Lett.*, 1986, 567.
3 K. Eguchi, T. Tokiai and H. Arai, *Appl. Catal.*, 1987, **34**, 275.
4 B. R. James and J. Louie, *Inorg. Chim. Acta*, 1969, **3**, 568.
5 R. C. Bohinski, *Modern Concepts in Biochemistry*, 5th edn., Allyn & Bacon, Boston, 1987, pp. 540–544.
6 N. A. Bzhasso and M. P. Pyatnitskii, *Zh. Prikl. Khim.*, 1969, **42**, 1610.
7 C. M. Jensen and W. C. Trogler, *Science*, 1986, **233**, 1069; D. Ramprasad, H. J. Yue and J. A. Marsella, *Inorg. Chem.*, 1987, **27**, 3151.
8 G. W. Bushnell, K. R. Dixon, R. G. Hunter and J. J. McFarland, *Can. J. Chem.*, 1972, **50**, 3694.
9 D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855.
10 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1987, pp. 173–176.
11 K. Hiraki, N. Ochi, H. Takaya, Y. Fuchita, Y. Shimokawa and H. Hayashida, *J. Chem. Soc., Dalton Trans.*, 1990, 1679.