Tetrahedron Letters, Vol. 34, No. 1, pp. 59-62, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

MILD REDUCTION OF α,β-UNSATURATED KETONES AND ALDEHYDES WITH AN OXYGEN-ACTIVATED PALLADIUM CATALYST

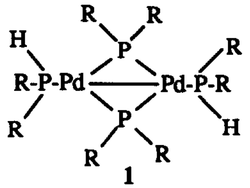
Milena Sommovigo and Howard Alper*
Ottawa-Carleton Chemistry Institute
Department of Chemistry University of Ottawa
Ottawa, Ontario, Canada K1N 6N5.

Summary: Reaction of the binuclear palladium complex, $[(R_2PH)PdPR_2]_2$, where R=t-Bu, with oxygen gives a very efficient catalyst for the hydrogenation of α,β-unsaturated carbonyls.

The selective hydrogenation of the carbon-carbon double bond of α,β-unsaturated ketones and aldehydes is an important goal in organic chemistry.[1] One strategy for effecting this transformation involves the use of metals or metal complexes as catalysts. Although good results can be achieved , especially for ketones, using metallic Pd as the catalyst, extensive studies have also been performed on homogeneous systems.[1-3] It is a well known fact that problems can arise, using heterogeneous catalysts, when the substrates are sensitive to hydrogenolysis or isomerization. Moreover, the effectiveness of such catalysts is strongly influenced by many factors such as the method of catalyst preparation, source of metal, solvent, amount of catalyst utilized, etc.[4]

Different catalytic systems have been used in recent years. For example, the hydride cluster, $[(Ph_3P)CuH]_6$, was found to be a versatile catalyst for the reduction of both α,β-unsaturated ketones[5] and aldehydes[6], affording the saturated carbonyl compounds in good yield and selectivity, under a high pressure of hydrogen. Good results have also been obtained using $(Cy_3P)_2Rh(H)(Cl)_2$ under biphasic conditions.[7] Other recent results include the use of Rh(I)/tris(m-sulfophenyl)phosphine trisodium salt,[8] and $PdCl_2$/ferrocenylamine sulfide complexes.[9] These systems also require hydrogen pressure and high temperatures. Low yields and low chemoselectivities have been reported using $Ru_3(CO)_{12}$/phosphine or phosphite complexes as catalysts for the reduction reaction.[10]

We now wish to report the selective hydrogenation of the carbon-carbon double bond of α,β-unsaturated ketones and aldehydes under very mild conditions, by use of a new class of palladium complexes, containing bulky bridging and terminal phosphine ligands, as catalyst precursors. Specifically, complex **1**[11], containing bridging $P(t\text{-}Bu_2)_2$ and terminal $P(t\text{-}Bu_2)_2H$ units, was evaluated as the catalyst for the noted conversion.



1

R=Bu^t

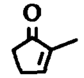
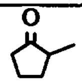
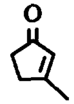
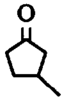
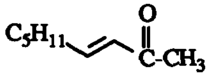
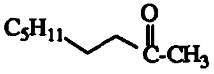
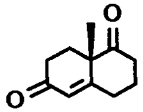
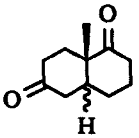
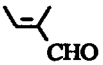
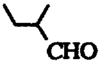
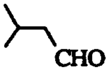
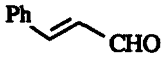
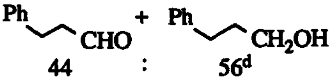
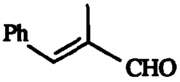
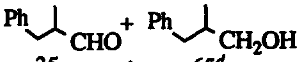
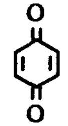
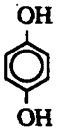
In a typical reaction, 1.5 mmol of 2-methyl-2-cyclopenten-1 one was quantitatively transformed into 2-methylcyclopentanone in the presence of 2% of **1** in tetrahydrofuran (THF) after reaction for 10 hours at room temperature under 10 psi of hydrogen (glass autoclave). Unfortunately the reaction was erratic, sometimes affording the saturated ketone in excellent yield, while little or no reaction occurred on other occasions. By a careful examination of the reaction conditions it was discovered, surprisingly, that the catalyst was not **1**, but an active species generated by reaction between **1** and traces of oxygen, present in the apparatus whenever purging with hydrogen was incomplete.

A yellow solution, obtained by bubbling oxygen through a suspension of **1** in THF and stirring overnight, was found to be an extremely active catalyst for the reduction. Using this catalytic system, quantitative conversion of 2-methyl-2-cyclopenten-1-one was achieved in only two hours, at 10 psi of H_2. The result was reproducible. In contrast, when the procedure was carried out using standard Schlenk techniques (rigorous exclusion of oxygen), no reaction was detected even after 18 hours under 10 psi of hydrogen.

The reduction of 2-methyl-2-cyclopenten-1-one, catalyzed by the complex generated from **1** and oxygen, could be affected in 98% yield, after six hours at room temperature under one atmosphere of hydrogen (compared to two hours at 10 psi of hydrogen). These conditions were applied with success to α,β-unsaturated ketones and aldehydes, and the results are listed in Table 1. Excellent results were obtained from ketones containing a di- or trisubstituted double bond, using 1-2% of **1**. The trisubstituted aldehydes, 2-methyl-2-butenal and 3-methyl-2-butenal, were also reduced chemospecifically at the double bond affording 2-methylbutanal and 3-methylbutanal in 95% and 90% yield, respectively. Cinnamaldehyde and its α,β-methyl analogue were also hydrogenated in good yield, but both the saturated aldehyde and alcohol were formed in these reactions. It is well known that unsaturated aldehydes, containing a phenyl group in conjugation, can undergo quite facile carbonyl as well as double bond reduction.[12] Finally, p-benzoquinone was converted to hydroquinone under the reaction conditions, aromatization being an apparent driving force for this reaction.[13]

The following procedure for 3-nonen-2-one is representative: the catalyst was prepared by adding 0.024 g (0.03 mmol) of **1** to THF (5 mL) in a standard Schlenk flask; the suspension was saturated with oxygen by bubbling the gas for two minutes through the solution, and stirring overnight at room temperature

TABLE 1 Reduction of α,β-Unsaturated Carbonyls Catalyzed by the Complex Generated from 1 and Oxygen.[a]

Entry	Substrate	Mol % of 1	Time (h)	Product(s)[b]	Yield[c]
1		1	6		(98)
2		2	18		90
3		2	10		97
4		1	12		83
5	Cholest-4-en-one	1	12	Cholestan-3-one	86
6		1	6		(95)
7		1	6		(90)
8		1	14	 44 : 56[d]	80
9		2	15	 35 : 65[d]	84
10		1	3		84

[a] See text for the general procedure. [b] Products were identified by comparison of spectral data (IR, NMR, MS) and GC retention times with those for authentic materials. [c] Isolated yields except for figures in parenthesis which are GC yields determined using an internal standard. [d] Ratio determined by NMR.

affording a clear yellow solution. The same flask was then evacuated and filled with hydrogen (one atmosphere). The substrate (0.21 g., 1.5 mmol) was then added and the reaction was monitored by gas-chromatography. After 10 hours, the reaction mixture was filtered (celite) and the filtrate was concentrated by rotary evaporation. The pure product (0.206 g., 97%) was isolated by Kugelrohr distillation and characterized by IR, ^{1}H NMR, and mass spectrometry.

In conclusion, the reaction of 1 with oxygen gives a complex which, although it has eluded isolation, is an excellent catalyst for the reduction of the double bond of unsaturated ketones and aldehydes.

Acknowledgments

We are grateful to British Petroleum, NATO (Collaborative Research Grant) and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We thank Dr. N. Satyanarayana for initial experiments.

References

1. Larock, R. C.; Comprehensive Organic Transformations: A Guide to Functional Group Preparations; VCH Publisher: New York, **1989.**
2. Colquhoun, H.M.; Holton, J.; Thompson, D.J.; Twigg, M. V.; New Pathways for Organic Synthesis. Practical Application of Transition Metals; Plenum Press: New York, **1984.**
3. James, B. R.; Homogeneous Hydrogenation; Wiley: New York, **1973.**
4. Russel, T. W.; Duncan, D. M.; Hansen, S.C.; *J. Org. Chem.* **1977,** *42,* 551 and references cited therein.
5. a) Mahoney, W. S.; Stryker, J. M.; *J.Am.Chem.Soc.* **1989,** *111,* 8818 ; b) Koenig, T. M.; Daeuble, J. F.; Brestensky, D. M.; Stryker, J. M.; *Tetrahedron Lett.* **1990,** *31,* 3237.
6. Brestensky, D. M.; Stryker, J. M.; *Tetrahedron Lett.* **1989,** 30, 5677.
7. Grushin, V. V.; Alper, H.; *Organometallics,* **1991,** *10,* 831.
8. Grosselin, J.M. ; Mercier, C.; Allmang, G.; Grass, F.; *Organometallics* **1991,** *10,* 2126.
9. Ali, H. M.; Naiini, A. A.; Brubaker, C. H. Jr; *Tetrahedron Lett.* **1991,** *32,* 5489.
10. Lau, C. P.; Ren, C.Y.; Chu, M.T.; Yeung, C. H.; *J. Mol. Catal.* **1991,** *65,* 287.
11. Leoni, P.; Sommovigo, M.; Pasquali, M.; Sabatino, P.; Braga, D.; *J. Organomet. Chem.* **1992,** *423,* 263.
12. Rylander, P. N.; Hydrogenation Methods; Academic Press, New York **1985.**
13. Hyatt, J. A.; *J. Org. Chem.* **1983,** *48,* 129

(Received in USA 2 September 1992; accepted 2 October 1992)