Tetrahedron Letters,Vol.26,No.19,pp 2263-2264,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

PALLADIUM CHLORIDE AND POLYETHYLENE GLYCOL PROMOTED OXIDATION OF TERMINAL AND INTERNAL OLEFINS

Howard Alper[a]*, Krzysztof Januszkiewicz[a], and David J.H. Smith[b]
[a]Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4
[b]B.P. Research Centre, Sunbury-on-Thames, Middlesex, U.K. TW16 7LN

Summary: Both terminal and internal olefins can be efficiently converted to ketones in polyethylene glycol and water using palladium chloride as the catalyst.

Recently, we described the application of phase transfer catalysis to the palladium catalyzed oxidation of olefins to ketones[1]. This is a useful reaction for terminal olefins, since the conditions are mild and the yields are good. However, internal olefins fail to react under these conditions.

Polyethylene glycols (PEG) have been employed as phase transfer agents and as solvents for promoting a variety of reactions[2] including the alkoxylation of halobenzenes[3] and the reduction of alkynes by sodium borohydride and palladium chloride.[4] The fact that polyethylene glycols are cheap makes them attractive from an industrial viewpoint. It seemed conceivable to us that the application of PEG[s] to the palladium(II) catalyzed olefin oxidation reaction would result in enhanced reactivity compared with the phase transfer process with quaternary ammonium salts. We now wish to report that both terminal and internal olefins are oxidized to ketones using polyethylene glycols.

When 1-decene was exposed to oxygen in a mixture of PEG-400 and water, with palladium chloride used as the catalyst and cupric chloride as re-oxidant [25 mmol/1mmol/10 mmol/20ml/1.5 ml ratio of 1-decene/$PdCl_2$/$CuCl_2$/PEG/H_2O], ketones were formed in 68% yield. Although the predominant product was 2-decanone, small amounts of isomeric decanones were also formed (see Table 1 for data). Increasing the proportion of water or decreasing the concentration of cupric chloride results in reduced product yields; however the distribution of isomeric ketones is similar. Of particular note are the observations that palladium trifluoroacetate is as good a catalyst as the metal chloride, and that the oxidation state of copper [i.e., CuCl vs. $CuCl_2$] influences the product distribution but not the yield of ketones. For a given set of conditions, the yield of decanones decreases if the chain length of PEG increases (PEG-1000) or decreases (PEG-200).

The PEG system enables one to effect olefin oxidation in a more facile manner than the phase transfer case. The formation of isomeric decanones from 1-decene suggests that the latter is undergoing isomerization to internal decenes and subsequent oxidation affords the various decanones. Indeed, internal olefins are oxidized in the presence of PEG-400 (Table 2). It is interesting to note that 2- and 3- but not 4- or 5-ketones were generated by oxidation of *cis*-2-decene or trans-2-nonene. A valuable material is methyl ethyl ketone (butanone) which thus far has not been produced commercially directly from butenes.[5] It now can be isolated in 71-82% yield using 1-butene or *cis*-2-butene in PEG/H_2O.

It is important to stress that not only do internal olefins undergo oxidation using polyethylene glycol, but the rate of oxidation of terminal olefins is greater when compared with the use of quaternary ammonium salts as phase transfer agents. For example, the rate of PEG-400 induced oxidation of 1-decene is 3.1 times faster than cetyltrimethylammonium bromide catalyzed oxidation of the same substrate under the same conditions [$O_2/PdCl_2/CuCl_2$]. Therefore, PEG is superior for the oxidation of both terminal and internal olefins.

The following general procedure was used: to $CuCl_2 \cdot 2H_2O$ in water was added $PdCl_2$,PEG-400, and the substrate (see Tables 1 and 2 for proportions used). Oxygen was bubbled through the stirred reaction mixture at 65° (1 atm - except for butenes which were run at 200 psi) and when complete (followed by gc), work-up was effected as follows: (a) volatile ketones were isolated by distillation; (b) in other cases, an equal amount of water was added, the products were extracted with hexane, and the dried hexane extract was distilled.

Table 1

Oxidation of Terminal and Internal Olefins using $PdCl_2$ and PEG/H_2O

Substrate(s)	$S/PdCl_2/CuCl_2/PEG/H_2O$[a]	Yield,%[b]	Product distribution, %
1-butene	26.8/1/2/15/1	71	butanone, 100
3,3-dimethyl-1-butene	25/1/10/20/2	27	3,3-dimethyl-2-butanone, 100
cis-2-butene	26.8/1/2/15/1	82	butanone, 100
trans-2-nonene	25/1/2/20/2	62	2-nonanone, 63; 3-nonanone, 37
1-decene	25/1/10/20/1.5	68	2-decanone, 88; 3-decanone, 7 4,5-decanone, 5
	25/1/2(CuCl)/20/2	69	2-decanone, 46; 3-decanone, 25 4,5-decanone, 29
	25/1[$Pd(OCOCF_3)_2$]/2/20/2	70	2-decanone,85; 3-decanone, 9 4,5-decanone, 6
cis-2-decene	25/1/2/20/2	47	2-decanone, 60;3-decanone, 40
trans-5-decene	25/1/2/20/2	40	5-decanone, 100
1,9-decadiene	25/1/10/20/2		2,9-decanedione, 55 isomeric diones, 13 3-chloro-2,9-decanedione, 32

[a] Units are mmol/mmol/mmol/ml/ml. [b] Products were identified by comparison of retention times (gas chromatography) and spectral properties (ir, nmr, ms) with authentic materials.

Acknowledgement

We are grateful to British Petroleum, and to the Natural Sciences and Engineering Research Council of Canada, for support of this research.

1. K. Januszkiewicz and H. Alper, Tetrahedron Lett., 25, 5159 (1983).
2. G.W. Gokel, D.M. Goli, and R.A. Schultz, J. Org. Chem., 48, 2837 (1983).
3. R. Neumann and Y . Sasson, Tetrahedron, 39, 3437 (1983).
4. N. Suzuki, T. Tsukanaka, T. Nomoto, Y. Ayaguchi, and Y. Izawa, J. Chem. Soc., Chem. Commun., 515 (1983).
5. D.T. Thompson, Chem. Brit., 333 (1984).

(Received in USA 1 November 1984)