

Reduction reactions using a binuclear palladium complex catalyst precursor and di-tert-butyl peroxide

In Sik Cho, Howard Alper *

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Received 14 April 1995; accepted 3 July 1995

Abstract

The binuclear palladium complex, $[(\text{Bu}_2\text{PH})\text{PdPBu}_2]_2$, preactivated by treatment with di-tert-butyl peroxide, catalyzes the selective hydrogenation of the carbon–carbon double bond of α,β -unsaturated carbonyls, sulfones and phosphonates in THF at room temperature and 1 atm of hydrogen pressure.

Keywords: Binuclear complexes; Palladium; Selectivity; Hydrogenation; α,β -Unsaturated compounds; Carbonyls; Sulfones; Phosphonates; Butyl peroxide

1. Introduction

There are numerous catalytic methods for the selective hydrogenation of the carbon–carbon double bond in α,β -unsaturated carbonyl compounds [1]. The most important factors affecting this catalytic hydrogenation are the choice of metal, ligand and reaction conditions. Under mild conditions, selective hydrogenation of the carbon–carbon double bond of α,β -unsaturated ketones and aldehydes was achieved by the use of a catalyst generated from the reaction of the bulky binuclear palladium complex

$[(\text{Bu}_2\text{PH})\text{PdPBu}_2]_2$ (1) [2] with oxygen [3,4] ¹. This catalytic system was also very useful for the hydrogenation of α,β -unsaturated sulfones and phosphonates [5]. The binuclear palladium complex 1 was not active itself for the hydrogenation of α,β -unsaturated carbonyls, sulfones or phosphonates.

¹ The authors of ref. [4] isolated a complex on treatment of 1 and oxygen. They claimed that the complex was responsible for the catalytic hydrogenation of α,β -unsaturated carbonyls. Observations in our laboratory (R. Aldea, unpublished results) show that the catalytic activity of the complex is *significantly* less than that of a mixture of 1 and O_2 . Clearly another, as yet unidentified, compound may be responsible for the catalysis reported herein and in refs. [3] and [5].


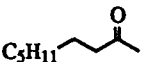

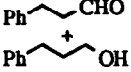
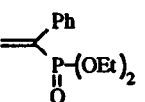
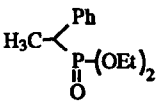
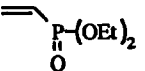
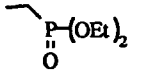
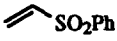
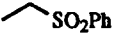
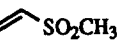
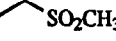
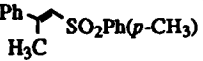
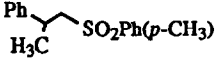
* Corresponding author.

Alternatives to employing molecular oxygen in these reactions were considered in order to avoid sequential use of two gases, and to compare the selectivity in reduction reactions. Previous studies have shown that di-tert-butyl perox-

ide is an effective substitute for oxygen in oxidative carbonylation reactions [6]. We now wish to report that the combination of 1 and di-tert-butyl peroxide results in the generation of an effective catalytic system for the selective re-

Table 1

Hydrogenation of α,β -unsaturated carbonyls, phosphonates and sulfones catalyzed by $[(\text{Bu}^t_2\text{PH})\text{PdPBu}^t_2]_2$ pretreated with oxygen (method A) or di-tert-butyl peroxide (method B)

Entry	Substrate ^a	Method	Mol % of catalyst	Reaction Time(hr)	Product	Isolated Yield(%)
1		A	2	10		97 ^b
		B	2	1		95
2		A	1	14		80(44:56) ^{b, c}
		B	1	6		79(73:27) ^c
3		A	2	0.5		88 ^d
		B	2	2		84
4		A	2	24		75 ^d
		B	2	18		72
5		A	2	5		83 ^d
		B	2	6.5		25
6		A	2	1		83 ^d
		B	2	2		79
7		A	4	4		93 ^d
		B	4	30		60

^a The unsaturated phosphonates and sulfones were prepared as described in refs. [7] and [8].

^b Ref. [3]

^c The ratio of aldehyde to alcohol was determined by ¹H-NMR.

^d Ref. [5].

duction of the double bond of α,β -unsaturated aldehydes, ketones, phosphonates, and sulfones affording the saturated products in good yields.

2. Results and discussion

The catalytically active system was generated by treatment of the binuclear palladium complex, **1**, with di-*tert*-butyl peroxide in tetrahydrofuran (THF) at 60°C for 30 min. Addition of the substrate and hydrogen, at room temperature and one atmosphere, afforded the product. These reactions were affected using a 25–100/1 ratio of substrate to **1**, with reaction times of 1–30 h, and the results are presented in Table 1.

The α,β -unsaturated ketone, 3-nonen-2-one (Table 1, entry 1), underwent facile hydrogenation using a 50/1 ratio of substrate/1, affording 2-nonanone in 95% isolated yield. The yield of product was comparable to that using 1/O₂, but the time required for completion of the reaction was appreciably less in the case of di-*tert*-butyl peroxide (1 h vs. 10 h using O₂). The reduction of cinnamaldehyde (entry 2) was also faster using di-*tert*-butyl peroxide than oxygen and the selectivity for 3-phenylpropanal was higher in the case of the peroxide. Although saturated phosphonates were isolated in similar yields from their α,β -unsaturated precursors (entries 3, 4), the reactions were more rapid using oxygen. While 1/((CH₃)₃CO)₂ is active for the hydrogenation of vinyl sulfones (entries 5–7), the reactions are less facile than those using 1/O₂, and the product yields are lower as well.

Note that the ratio of di-*tert*-butyl peroxide to **1** in these reactions was 10/1. This ratio was used simply for the convenience of handling. For example, use of only a 2:1 ratio of [(CH₃)₃CO]₂/1 in the reduction of 3-nonen-2-one afforded 2-nonanone in 92% yield [compare with 95% yield using 10:1 ratio (Table 1, entry 1, method B)].

In conclusion, the catalytic system generated *in situ* from **1** and di-*tert*-butyl peroxide is

effective for the operationally simple and mild selective hydrogenation of the carbon–carbon double bond in α,β -unsaturated carbonyls, sulfones and phosphonates in good yields. This methodology is superior (α,β -unsaturated carbonyls), comparable (phosphonates), or inferior (sulfones) to that involving **1** and oxygen.

3. Experimental

3.1. General

¹H-NMR spectra were obtained on a Gemini 200 MHz spectrometer using CDCl₃, as the solvent and Me₄Si as the internal standard. A VG 7070E spectrometer was used for mass spectral determinations. GC analyses were carried out on a Varian star 3400 instrument, equipped with a column packed with 1.5% OV-17 + OV-210 on Chromosorb W-HP (100–120 mesh).

3.2. Typical procedure for the hydrogenation of α,β -unsaturated carbonyls, sulfones and phosphonates

Di-*tert*-butyl peroxide (15 mg, 0.1 mmol) was added to a solution of THF (5 ml) containing **1** (8 mg, 0.01 mmol). The solution was stirred for 30 min at 60°C and became clear yellow. 3-Nonen-2-one (70 mg, 0.5 mmol) was added to the catalytic solution, and hydrogen was bubbled through the stirred reaction mixture at room temperature. The reaction was monitored by gas chromatography, and after 1 h, the reaction was filtered through neutral alumina and the solvent was removed by rotary evaporation. 2-Nonanone (67 mg, 95%) was isolated by distillation and characterized by comparison of spectral data [IR, NMR(¹H, ¹³C), MS] with those for an authentic sample.

Acknowledgements

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

References

- [1] H. Takaya and R. Noyori, in B.M. Trost (Ed.), *Comprehensive Organic Synthesis*, Vol. 8, Pergamon Press, New York, 1991, Chapter 3.2, p. 452–453.
- [2] P. Leoni, M. Sommovigo, M. Pasquali, P. Sabatino and D. Braga, *J. Organomet. Chem.*, 423 (1992) 263.
- [3] M. Sommovigo and H. Alper, *Tetrahedron Lett.*, 34 (1993) 55.
- [4] P. Leoni, F. Marchetti and M. Pasquali, *J. Organomet. Chem.*, 451 (1993) C25.
- [5] I.S. Cho and H. Alper, *J. Org. Chem.*, 59 (1994) 4027.
- [6] H. Alper, G. Vasapollo, F.W. Hartstock, M. Mlekuz, D.J.H. Smith and G.E. Morris, *Organometallics*, 6 (1987) 2391. G.E. Morris, D. Oakley, D.A. Pippard and D.J.H. Smith, *J. Chem. Soc., Chem. Commun.*, (1987) 410, 411.
- [7] N. Kamigata, H. Sawada and M. Kobayashi, *Chem. Lett.*, (1979) 159.
- [8] T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Tetrahedron Lett.*, 21 (1980) 3595.