ELSEVIER

Aerobic oxidation of trivalent phosphorus and arsenic compounds in the presence of 3-methylbutanal and metal catalyst

Piero Mastrorilli, Francesco Muscio, Cosimo Francesco Nobile [*], Gian Paolo Suranna

Centro di Studi CNR sulle Metodologie Innovative in Sintesi Organiche M.I.S.O., Istituto di Chimica del Politecnico di Bari, trav.200 Re David, 4 I-70126 Bari, Italy

Abstract

The oxidation of alkyl and aryl phosphines, tryphenylphosphite and triphenylarsine was achieved using oxygen or air as the oxidant in the presence of excess 3-methylbutanal and catalytic amount $Co(acac)_2$. Tests carried out with a heterogeneous analogue of $Co(acac)_2$ revealed that the supported cobalt polymer acts as an active and reusable catalyst in the oxidation of triphenylphosphine. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Phosphine oxides preparation and synthetic applications are of utmost importance in organic chemistry. They are important synthones for a number of organic reactions, such as the Horner–Wittig reaction [1] or several coupling [2,3], alkylation [4], acylation [5–8] or addition [9–11] reactions, all of them triggered by an α-phosphinoyl carbanion.

Noteworthy among the most recent examples of catalytic oxidation of phosphorus compounds are those based on $FeCl_3/H_2O_2$ [12], CH_3-ReO_3/O_2 [13] and Ru-porphyrine/O_2 [14].

Pursuing our studies on the aerobic oxidation of organic substrates using the catalytic system based on a metal acetylacetonate, a sacrificial aldehyde and oxygen or air [15–20], we recently became interested in the oxyfunctionalization of trivalent phosphorus and arsenic compounds leading to pentavalent species.

2. Experimental

2.1. Materials and apparatus

The metal acetylacetonates, the substrates, the standards and 3-methylbutanal were purchased by Aldrich. Chromatographic analyses were carried out on a Hewlett Packard 6890

---

[*] Corresponding author. Tel.: +39-80-546-0608; Fax: +39-80-546-0604

Table 1
Oxidation of triphenylphosphine (2.42 mmol) with dioxygen ($p = 1$ atm), 3-methylbutanal (1.85×4 mmol added at times = 0, 3, 6 and 9 h), t-butylhydroperoxide (5% respect to the substrate) in 1, 2-dichloroethane (2.0 ml) at room temperature

Entry	Catalyst	Time (h)	Yield (%)
1	none	48	46
2	Cu(acac)$_2$	48	88
3	Ni(acac)$_2$	24	92
4	Pd(acac)$_2$	48	94
5	Fe(acac)$_3$	24	100
6	Co(acac)$_2$	12	100
7	supported cobalt	12	100
8[a]	supported cobalt	13	100

Catalyst/substrate = 1/60 mol/mol.
[a]Recycle of the previous run.

instrument using a capillary 30 m HP-5 (5% phenyl methyl siloxane) column or a capillary 30 m SPB-1 column. GCMS data were acquired on a HP 5973 instrument. HPLC analyses were carried out by a LC-10AD Shimadzu instrument using a 25 cm Spherisorb 5-C8 column and CH_3CN/H_2O mixtures as eluent. The oxidised products were identified by comparison of their MS spectra and retention times in GC (HPLC) analyses with those of authentic samples.

Conversions and yields were calculated by GLC or HPLC analyses as moles of oxidised product per mole of starting substrate by using the internal standard method.

2.2. Catalytic runs

2.2.1. Homogeneous phase

A Schlenk tube wrapped with aluminium foil was charged with the substrate, the metal acetylacetonate (when present), 3-methylbutanal (ad-

ded as specified in the captions of the tables) and t-butylhydroperoxide (5% respect to the substrate) in 1,2-dichloroethane (2 ml) and vigorously stirred under dioxygen or air ($p = 1$ atm) at room temperature (21°C), and monitored by GLC or HPLC and GCMS.

2.2.2. Heterogeneous phase

A Schlenk tube wrapped with aluminium foil was charged with triphenylphosphine (2.42 mmol), the supported cobalt catalyst (50.1 mg, 4.47% of Co), 3-methylbutanal (added as specified in the caption of Table 1) and t-butylhydroperoxide (5% respect to triphenylphosphine) in 1,2-dichloroethane (2 ml) and vigorously stirred under dioxygen ($p = 1$ atm) at room temperature until completion of the reaction as monitored by GLC. The supported catalyst was recovered after duty by addition of petroleum ether to the suspension and subsequent centrifugation. The recovered resin was washed with acetone and diethyl ether, dried under vacuum and recycled.

3. Results and discussion

3.1. Oxidation of triphenylphosphine

Triphenylphosphine was submitted to oxidative conditions in the presence of several different metal catalysts. The relevant results are summarised in Table 1. It is apparent that the non-catalysed reaction was significantly slower than all the catalysed ones. Among the metal

Table 2
Oxidation of P(OPh)$_3$ and AsPh$_3$ (2.42 mmol) with dioxygen ($p = 1$ atm), 3-methylbutanal (1.85×4 mmol added at times = 0, 3, 6, 9 h), t-butylhydroperoxide (5% respect to the substrate) in 1,2-dichloroethane (2.0 ml) at room temperature

Entry	Substrate	Catalyst	Time (h)	Conversion (%)	Selectivity (%)	Product
1	P(OPh)$_3$	none	32	59	32	OP(OPh)$_3$
2	P(OPh)$_3$	Co(acac)$_2$	32	62	60	OP(OPh)$_3$
3	AsPh$_3$	none	24	9	100	OAsPh$_3$
4	AsPh$_3$	Co(acac)$_2$	24	96	100	OAsPh$_3$

Co(acac)$_2$/substrate = 1/60 mol/mol.

Table 3

Oxidation of air sensitive phosphines (0.6 mmol) with dry air (p = 1 atm), 3-methylbutanal (0.46×3 mmol added at times = 0, 15, 30 min for methods b and c), t-butylhydroperoxide (5% respect to the substrate) in 1,2-dichloroethane (2.0 ml) at room temperature

Entry	Substrate	Oxidative conditions	Time (min)	Conversion (%)	Selectivity(%)	Product
1	PPh_2H	a	90	94	92	$OPPh_2H$
2	PPh_2H	b	20	95	100	$OPPh_2H$
3	PPh_2H	c	60	57	88	$OPPh_2H$
4	PCy_3	a	45	98	63	$OPCy_3$
5	PCy_3	b	15	98	85	$OPCy_3$
6	PCy_3	c	80	99	95	$OPCy_3$

$Co(acac)_2$/substrate = 1/60 mol/mol.

Conditions: (a) dry air without aldehyde; (b) dry air with aldehyde; (c) dry air, aldehyde, $Co(acac)_2$.

acetylacetonates tested, the Co(II) one was shown to be the most active catalyst, affording quantitative conversion in 12 h.

The insoluble resin containing supported $Co(AAEMA)_2$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] was tested as heterogeneous catalyst in the oxidation of triphenylphosphine. This resin is easily synthesised [21] from $Co(AAEMA)_2$, methylenebisacrylamide and dimethylacrylamide in dimethylformamide, and resulted active and recyclable in the aerobic oxidation of sulfides [22] and of hydroxyketones [23].

The results obtained in the oxidation of triphenylphosphine in the heterogeneous phase (entries 7 and 8 of Table 1) show that the heterogeneous catalyst exhibited comparable activity respect with its homogeneous analogue and is recyclable with negligible loss of activity.

3.2. Oxidation of triphenylphosphite and triphenylarsine

Triphenylphosphite was oxidised to triphenylphosphate in the presence of $Co(acac)_2$ as metal catalyst. Results summarised in Table 2 (entries 1 and 2) show that non-catalysed and catalysed processes afford comparable conversions but significantly different selectivities. The main side product found in the reaction solution is phenol, probably deriving from homolytic cleavage of the P–OPh bond.

As to triphenylarsine, the reaction carried out in the presence of the metal catalyst (Table 2,

entry 4) gave excellent selectivity and almost complete conversion. The non-catalysed reaction, on the contrary, was exceedingly slow (entry 3).

3.3. Oxidation of tricyclohexylphosphine and diphenylphosphine

The oxidation of these two air sensitive phosphines was carried out under three different oxidative conditions, namely: (a) stirring under dry air (p = 1 atm), (b) stirring in the presence of excess sacrificial aldehyde under dry air (p = 1 atm), (c) stirring in the presence of excess sacrificial aldehyde and $Co(acac)_2$ under dry air (p = 1 atm). All reactions were triggered by t-butylhydroperoxide (5% respect to the sub-
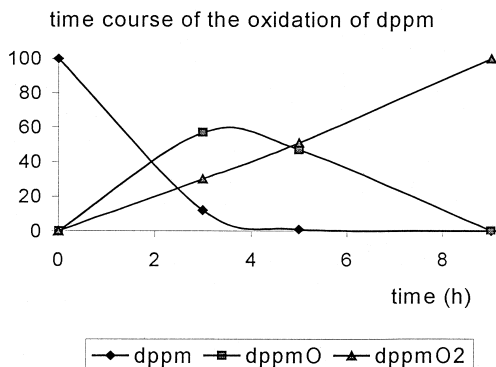

Fig. 1. Oxidation of diphenylphosphinomethane (0.25 mmol) with air (p = 1 atm), 3-methylbutanal (0.37×4 mmol added at times = 0, 3, 6, 9 h), t-butylhydroperoxide (5% respect to the substrate) in 1, 2-dichloroethane (2.0 ml) at room temperature; catalyst/substrate = 1/30 mol/mol.

Table 4
Aerobic oxidation of dppm and dppe (0.25 mmol) in the presence of 3-methylbutanal, *t*-butylhydroperoxide (5% respect to the substrate) in 1,2-dichloroethane (2.0 ml) at room temperature and atmospheric pressure

Entry	Substrate	Oxidant	Catalyst	Time (h)	Conversion (%)	% monoxide	% dioxide
1[a]	dppm	air	none	9	18	70	30
2[b]	dppm	air	$Co(acac)_2$	3	88	65	35
3[c]	dppm	O_2	$Co(acac)_2$	6	100	–	100
4[d]	dppe	air	none	5	8	100	–
5[e]	dppe	air	$Co(acac)_2$	2.2	100	55	45
6[f]	dppe	O_2	$Co(acac)_2$	2	100	–	100

$Co(acac)_2$/substrate = 1/30 mol/mol.
[a] 0.37×3 mmol aldehyde added at times = 0, 3 and 6 h.
[b] 0.37 mmol aldehyde present at the beginning of the reaction.
[c] 0.37×2 mmol aldehyde added at times = 0 and 3 h.
[d] 0.19×4 mmol aldehyde added at times = 0, 0.67, 3 and 4 h.
[e] 0.19×4 mmol aldehyde added at times = 0, 40, 60 and 90 min.
[f] 0.74×2 mmol aldehyde added at times = 0 and 1 h.

strate). The results summarised in Table 3 show that in the case of PPh_2H the simple exposition to air transforms most of the substrate into the corresponding P-oxide, the reaction being accelerated by the presence of the sacrificial aldehyde (entries 1 and 2). The metal catalysed reaction gave the worst result in terms of both conversion and selectivity. The oxidation of tricyclohexylphosphine with method (a) was quite fast but rather unselective (entries 4 and 5), main side products being $OP(OCy)Cy_2$ and $OP(OCy)_2Cy$. Metal catalysed oxidation (method c) gave the best result in terms of yield in tricyclohexylphosphineoxide (94% after 80 min, entry 6). The slowing down of the reaction caused by the presence of $Co(acac)_2$ can be tentatively ascribed to the formation of an in situ complex between the basic PPh_2H or PCy_3 phosphines and the cobalt, that could act as an inhibitor towards the formation of the radical species responsible for the oxidation.

3.4. Oxidation of diphenylphosphinomethane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe)

The time course of the oxidation of dppm carried out using air as the oxidant is depicted in Fig. 1. It is apparent that after 9 h the reaction affords selectively the dioxide. After 3 h reaction the solution contains 57% of diphenylphosphinomethanemonoxide. Quantitative conversion of the diphosphine into dioxide could also be obtained under dioxygen after 6 h reaction (entry 3 of Table 4).

When dppe was submitted to oxidative conditions, quantitative yield of the corresponding dioxide was obtained after 2 h reaction under a pure dioxygen atmosphere. Using air instead of O_2 it was possible to stop the oxidation when the reaction mixture contained 55% monoxide and 45% dioxide (entry 5 of Table 4). Remarkably, both diphosphines reacted sluggishly in the absence of cobalt catalyst (entries 1 and 4).

References

[1] B.E. Maryanoff, A.B. Reitz, Chem. Rev. 89 (1989) 863.
[2] C.A. Maryanoff, B.E. Maryanoff, R. Tang, K. Mislow, J. Am. Chem. Soc. 95 (1973) 5839.
[3] T. Minami, Y. Okada, R. Nomura, S. Hirota, K. Fukuyama, Chem. Lett. (1986) 613.
[4] K.M. Pietrusiewicz, M. Zablocka, J. Monkiewics, J. Org. Chem. 49 (1984) 1522.

[5] R.S. Torr, S. Warren, J. Chem. Soc. Perkin Trans. 1 (1983) 1173.

[6] G. Keglevich, I. Petnehàzy, P. Miklos, A. Almasy, G. Toth, L. Toke, L.D. Quinn, J. Org. Chem. 52 (1987) 3983.

[7] J.J. Richard, V. Banks, J. Org. Chem. 28 (1963) 123.

[8] C.A. Cornish, S. Warren, J. Chem. Soc. Perkin Trans. 1 (1985) 2585.

[9] C.R. Johnson, T. Imamoto, J. Org. Chem. 52 (1987) 2170.

[10] R.K. Haynes, S.C. Vonwiller, J. Chem. Soc. Chem. Commun. (1987) 92.

[11] R.K. Haynes, A.G. Katsifis, Aust. J. Chem. 42 (1989) 1473.

[12] D.H. Barton, D.R. Hill, B. Hu, Tetrahedron 38 (1997) 1711.

[13] Z. Zhu, J.H. Espsnson, J. Mol. Catal. A 103 (1995) 87.

[14] B.R. James, Catalysis of Organic Reactions, in: W.E. Pascoe (Ed.), Marcel Dekker, New York, 1992, p. 245.

[15] P. Mastrorilli, C.F. Nobile, Tetrahedron Lett. 35 (1994) 4193.

[16] L. Lopez, P. Mastrorilli, G. Mele, C.F. Nobile, Tetrahedron Lett. 35 (1994) 3633.

[17] R. Giannandrea, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. 99 (1994) 27.

[18] P. Mastrorilli, C.F. Nobile, J. Mol. Catal. 99 (1994) 19.

[19] P. Mastrorilli, C.F. Nobile, G.P. Suranna, L. Lopez, Tetrahedron Lett. 51 (1995) 7943.

[20] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A 130 (1998) 65.

[21] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A 130 (1995) 17.

[22] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A 108 (1996) 57.

[23] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, L. Lopez, J. Mol. Catal. A 111 (1996) 33.