ELSEVIER

Oxyfunctionalization of hydrocarbons by in situ formed peracid or by metal assisted aerobic oxidation

Maria M. Dell'Anna, Piero Mastrorilli, Cosimo F. Nobile [*]

Centro di studi CNR sulle Metodologie Innovative in Sintesi Organiche, Istituto di Chimica del Politecnico di Bari, Trav. 200 Re David, 4, 70126 Bari, Italy

Abstract

The oxidation of hydrocarbons such as adamantane, cyclohexane, tetraline and indane has been investigated using the oxygen/3-methylbutanal system in the presence and in the absence of metal catalyst. The reactivity order reflects the facility of hydrogen abstraction from the substrate. © 1998 Elsevier Science B.V.

Keywords: Oxidation; Alkanes; Hydrocarbons; Metal β-diketonates; Sacrificial aldehyde; Peracid

1. Introduction

Alkane functionalization has achieved in the last years growing attention from both the synthetic and biological point of view [1–8].

Among the most recent examples of oxidation of the C–H bond in higher alkanes, those based on 2,6-dichloropyridine-*N*-oxide in the presence of ruthenium pentafluorophenylporphyrin [9], the O_2/H_2O_2/pyrazine-2-carboxylic acid/vanadate induced hydroperoxidations [10], the O_2/N-hydrophtalimide/cobalt acetylacetonate oxidations [11], those based on a metal/hydroperoxide system [12,13] or on heteropolyoxometalates [14,15] and the photo-

chemical oxidation of cyclohexane by O_2 in a zeolite [16] are noteworthy.

Murahashi et al. have recently reported the iron or ruthenium catalyzed oxidation of alkanes by molecular oxygen in the presence of aldehydes and acids [17], claiming a maximum conversion for the adamantane of 36%. Similar results were obtained using copper salts as catalysts [18].

Other examples of oxidations in which the synergic effect of the oxygen and an aldehyde as co-reductant was exploited in the activation of hydrocarbons have been reported, using cobalt(II) Schiff base complexes [19,20], or metalloporphyrins as catalysts [21–23].

In the framework of our study on aerobic oxidation of organic substrates catalyzed by dioxygenato complexes of transition metals in

---

[*] Corresponding author. Fax: +39-80-4560611.

the presence of sacrificial aldehydes [24–29], we have reported preliminary results obtained in the oxyfunctionalization of adamantane carried out in the presence of a catalytic amount of $M(AAEMA)_n$ ($AAEMA^- =$ deprotonated form of 2-(acetoacetoxy)ethyl methacrylate, M = Fe, $n = 3$; Ni, $n = 2$ and Co, $n = 2$) and excess 3-methylbutanal [25,26].

Here we disclose results obtained from the activation of C–H bonds in substrates such as adamantane, cyclohexane, tetraline and indane carried out in the presence or in the absence of metal catalysts. The achieved conversions range up to 81% in the case of adamantane and up to 100% in the case of tetraline and indane.

2. Results and discussion

The more frequently proposed mechanistic pathway for metal catalyzed oxidations of organic substrates in the presence of a co-reductant such as an aldehyde is the metal catalyzed oxidation of the aldehyde to a peracid species which consequently form a metal-oxo complex active in the oxygen transfer onto the substrate [27,30–32]. Moreover it is known that the autoxidation of the aldehyde in the absence of metal species can also give rise to peroxo-compounds able to oxidize alkenes [1,27,33] [1] and ketones [34,35].

Mizuno and Finke have recently claimed that the aerobic epoxidation of cyclohexene triggered by the aldehyde/O_2/polyoxoanion-supported catalyst system is rather unreproducible unless a radical initiator such as cyclohexenyl-hydroperoxide is added to the reaction mixture [36].

We have submitted adamantane, as a paradygmatic substrate, to different oxidative conditions with the aim of clarifying the com-

Table 1
Oxidation of adamantane (1.2 mmol) with 3-methylpropanal (14.4 mmol) at room temperature and 1 atm dioxygen. Reaction time = 70 h)

Entry	ROOH		Conv. (%)
1	no	dark	66 ± 24
2	no	light	70 ± 13
3	yes	dark	62 ± 3
4	yes	light	71 ± 3

bined effects of the metal catalyst, of the radical initiator and of the light.

As to the method of refurnishing the system of the aldehyde, one third of the aldehyde needed for the reaction to reach completion was present in the reaction mixture at the beginning of the reaction and the rest was added dropwise in two steps during the reaction (this procedure was used in all reactions described in this paper).

Table 1 shows the effects of light and of a radical initiator in the oxidation of adamantane carried out in the absence of metal catalyst. Each reaction was carried out five times.

It is apparent that the oxidation of adamantane proceeds even in the absence of metal catalyst (conversion, 62–71% after 70 h) and is only slightly affected by the light parameter, the reactions being a little faster when carried out in daylight.

The addition of a catalytic amount of *t*-butylhydroperoxide to the reaction mixture (entries 3 and 4) resulted in no substantial change in activity. The reproducibility, however, was considerably improved.

The distribution of the oxidation products was found to be similar in all non-catalysed reactions and dependent on the achieved conversion. The major product was 1-adamantanol, side-products being 1,3-dihydroxyadamantane and adamantolactone. A solution mixture analyzed after 70 h reaction (at 71% conversion) was made up of 73% 1-adamantanol, 16% 1,3-dihydroxyadamantane and 11% adamantolactone.

---

[1] See also note 7 of Ref. [24].
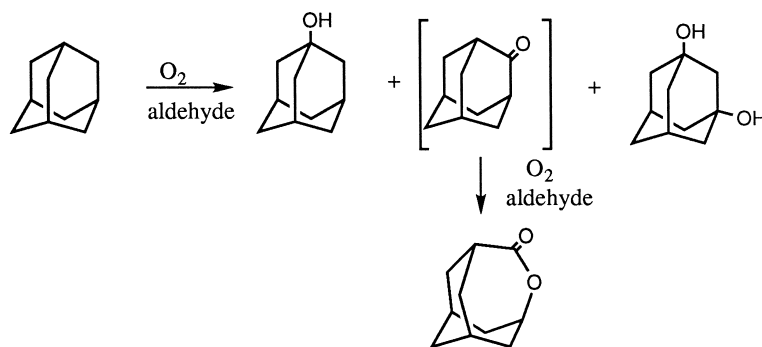
Scheme 1.

The scarce abundance (if not the absence) of 2-adamantanone in the reaction mixtures can be ascribed to its relatively fast overoxidation to the found lactone (Scheme 1) via a Bäyer–Villiger process. Fig. 1 shows a typical reaction course.

The results of reactions carried out in the presence of a metal acetylacetonate as catalyst are summarized in Table 2. The reactions were carried out in the dark and in the presence of 6.7% t-BuOOH (mol hydroperoxide/mol substrate). Among the tested metals, palladium, iron, nickel and cobalt gave the best results, affording 75–81% conversion of the substrate and 66–74% selectivity into 1-adamantanol (entries 1–4).

Cu(acac)$_2$ (entry 6) gave results comparable with those obtained in the absence of metal catalyst (entry 7) whereas Mn(acac)$_3$ was found to be the less selective catalyst (entry 5). In the case of cobalt, as well as in palladium and manganese catalysed reactions, the formation of a notable amount of 2,7-dimethyl-4,5-octandione (probably derived by the coupling of two 3-methyl-butanoyl radicals formed during reactions) was detected in the reaction mixture [37] [2]. Moreover, Mn(acac)$_3$ catalysed reaction mixtures contained a notable amount of 2-adamantanone (9% at 70% conversion, 6.3% yield) and adamantyl isovalerate (10% at 70% conversion, 7% yield), a unique case among those tested.

When cyclohexane was submitted to oxidative conditions the highest achieved conversion was that obtained using Co(acac)$_2$. After 24 h reaction, cyclohexane was converted selectively into cyclohexanone with 14% yield. Subsequent additions of aldehyde and prolonged reaction times did not produce any progress in the reaction. The yields obtained with catalysts such as Pd(acac)$_2$, Ni(acac)$_2$ and Fe(acac)$_2$, as well as those obtained in non-catalysed reactions were less than 3%.
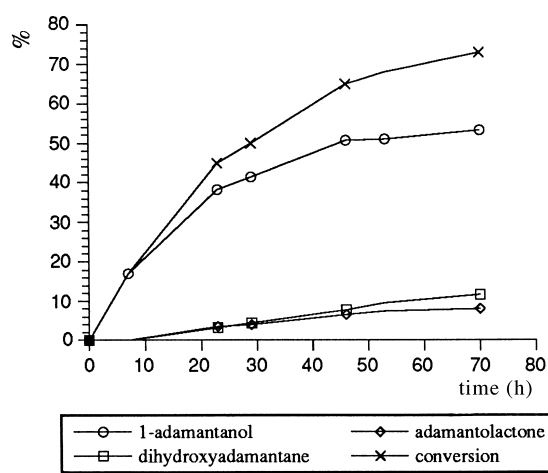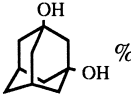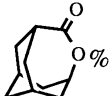

Fig. 1. Time course of adamantane oxidation (1.2 mmol) with 3-methylbutanal (14.4 mmol) and t-BuOOH (0.086 mmol) at room temperature and 1 atm dioxygen.

---

[2] The oxidative coupling of aliphatic aldehydes into symmetrical 1,2-diones catalysed by the acetic anydride/O$_2$/CoCl$_2$ system has been recently reported.

Table 2

Oxidation of adamantane (1.2 mmol) by metal acetylacetonate (0.020 mmol) with 3-methylbutanal (14.4 mmol) in the presence of *t*-butylhydroperoxide (0.086 mmol) in 1,2-dichloroethane in the dark at room temperature and 1 atm dioxygen; reaction time = 70 h

Entry	metal catalyst	conversion %	![OH structure] %	![OH/OH structure] %	![O/O structure] %
1[a]	Pd(acac)$_2$	81	66	18	13
2	Co(acac)$_2$	76	74	18	8
3	Fe(acac)$_3$	75	73	16	11
4	Ni(acac)$_2$	75	70	18	12
5	Mn(acac)$_3$	70	63	11	0
6	Cu(acac)$_2$	66	77	12	11
7	none	63	78	10	12

[a] Reaction time = 46 h.

Tables 3 and 4 summarize the results obtained in the oxidation of tetraline and indane. In both cases the reactions carried out in the absence of metal catalyst (entries 5) gave less conversions compared with those carried out with a metal catalyst.

The major product was, in all cases, the corresponding α-ketone, derived from over-oxidation of the corresponding alcohol, thus substantiating a higher reactivity of the initially formed benzylic alcohol compared to the substrate. Other side-products of these reactions (Scheme 2) were the lactone derived from oxidation of the α-ketone and the α,δ-diketone (only in the case of tetraline).

Although all tested metals gave satisfactory yields, nickel was found to be the most active catalyst in the oxidation of tetraline, whereas

Table 3

Oxidation of tetraline (1.2 mmol) by metal acetylacetonate (0.020 mmol) with 3-methylbutanal (14.4 mmol) in the presence of *t*-butylhydroperoxide (0.086 mmol) in 1,2-dichloroethane in the dark at room temperature and 1 atm dioxygen; reaction time = 70 h
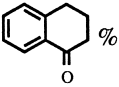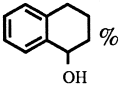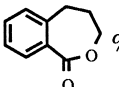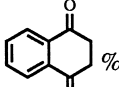
Entry	metal catalyst	conversion %	![ketone] %	![alcohol OH] %	![lactone] %	![diketone] %
1	Pd(acac)$_2$	84	80	5	8	7
2	Co(acac)$_2$	90	81	0	19	0
3	Fe(acac)$_3$	88	78	5	9	8
4	Ni(acac)$_2$	100	75	0	12	13
5	none	61	80	20	0	0

Table 4

Oxidation of indane (1.2 mmol) by metal acetylacetonate (0.020 mmol) with 3-methylbutanal (14.4 mmol) in the presence of *t*-butylhydro-peroxide (0.086 mmol) in 1,2-dichloroethane in the dark at room temperature and 1 atm dioxygen; reaction time = 54 h
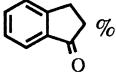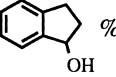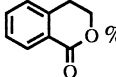
Entry	metal catalyst	conversion %	%	%	%
1	Pd(acac)$_2$	89	89	0	11
2[a]	Co(acac)$_2$	100	78	0	22
3	Fe(acac)$_3$	82	84	6	10
4	Ni(acac)$_2$	96	90	0	10
5	none	73	85	10	5

[a] Reaction time = 31 h in the presence of 9.6 mmol of 3-methylbutanal.

cobalt gave the best results (78% yield in in-danone after 31 h and only one addition of 3-methylbutanal) in the oxidation of indane.

The reactivity order of the four substrates under study, namely indane ≈ tetraline > adamantane > cyclohexane can be explained in terms of stability of the radical formed by abstraction of H· from the hydrocarbon. In fact the abstraction of a hydrogen atom from the

α-position in tetraline or indane gives rise to benzylic radicals stabilized by resonance. The facility of hydrogen abstraction in alkanes, moreover, depends on the type of carbon atom to which the hydrogen is bonded, tertiary carbon radicals being more stable compared to secondary or primary ones. This justifies the selectivity towards 1-adamantanol observed in the oxidation of adamantane (which contains

n=1, 2
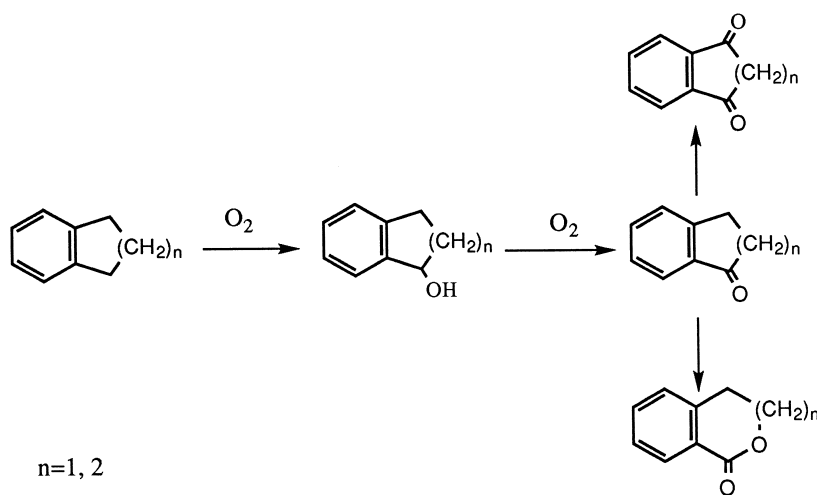
Scheme 2.

both secondary and tertiary C–H bonds) and the lack of reactivity of cyclohexane (which contains only secondary C–H bonds).

3. Experimental

3.1. Materials and apparatus

Chromatographic analyses were carried out on a Hewlett Packard 5890 instrument using a capillary 25 m SPB-1 column or a capillary 30 m Carbowax 20M column. GCMS data were acquired on a HP 5890 chromatograph (30 m SE30 or carbowax 20 m columns) coupled with a mass selective detector HP 5970B, 70 eV.

The oxidized products were identified by comparison of their MS spectra and retention times in GC analyses with those of authentic samples.

Conversions and yields were calculated by GLC analyses as moles of oxidized product per mole of starting alkane by using the internal standard method.

The metal acetylacetonates, hydrocarbons and 3-methylbutanal were purchased by Aldrich.

3.2. Catalytic runs

A Schlenk tube was charged with the substrate (1.2 mmol), the metal complex (0.020 mmol, when used) and 3-methylbutanal (0.90 mmol) in 1,2-dichloroethane (DCE, 4 ml for the oxidation of adamantane, 2 ml in the other cases) and vigorously stirred under dioxygen ($p = 1$ atm) at room temperature (21°C). 3.9 mmol aldehyde dissolved in 2 ml DCE were dropped in the reaction vessel at a rate of 2 mmol/h. After 24 and 48 h two more dropwise additions of 3.9 mmol aldehyde each were carried out. The reactions in the dark were carried out by wrapping both the reaction vessel and the dropping funnel containing the aldehyde with aluminium foil.

References

[1] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[2] C.L. Hill, Activation and Functionalization of Alkanes, Wiley, New York, 1989.
[3] L. Simandi, Catalytic Activation of Dioxygen by Metal Complexes, Kluwer Academic Publisher, Boston, 1992.
[4] D.H.R. Barton, A.E. Martell, D.T. Sawyer (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation, Plenum Press, New York, 1993.
[5] B. Mennier, Chem. Rev. 92 (1992) 1411.
[6] B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Chemistry, vol. 7.
[7] R.A. Sheldon (Ed.), Metalloporphirins in Catalytic Oxidations, Marcel Dekker, New York, 1994.
[8] F. Montanari, L. Casella (Eds.), Metalloporphirins Catalyzed Oxidations, Kluwer, Dordrecht, 1994.
[9] J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961.
[10] G.B. Shul'pin, M.C. Guerreiro, U. Schuchardt, Tetrahedron 52 (1996) 13051.
[11] Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, J. Org. Chem. 61 (1996) 4520.
[12] D.T. Sawyer, A. Sobkowiak, T. Matsushita, Acc. Chem. Res. 29 (1996) 409.
[13] J. Kim, R.G. Harrison, C. Kim, L. Que Jr., J. Am. Chem. Soc. 118 (1996) 4373.
[14] L. Ermolenko, C. Giannotti, J. Mol. Catal. 114 (1996) 87.
[15] Y. Matsumoto, M. Asami, M. Hashimoto, M. Misono, J. Mol. Catal. 114 (1996) 161.
[16] H. Sun, F. Blatter, H. Frei, J. Am. Chem. Soc. 118 (1996) 6873.
[17] S.I. Murahashi, Y. Oda, T. Naota, J. Am. Chem. Soc. 114 (1992) 7913.
[18] S.I. Murahashi, Y. Oda, T. Naota, N. Komiya, J. Chem. Soc. Chem. Commun. (1993) 139.
[19] T. Punniyamurthy, S.J.S. Kalra, J. Iqbal, Tetrahedron Lett. 36 (1996) 8497.
[20] G.C. Maikap, D. Guhathakurta, J. Iqbal, Synlett (1995) 189.
[21] S.I. Murahashi, T. Naota, N. Komiya, Tetrahedron Lett. 36 (1995) 8059.
[22] A.K. Mandal, V. Khanna, J. Iqbal, Tetrahedron Lett. 37 (1996) 8059.
[23] P. Battioni, R. Iwanejko, D. Mansuy, T. Mlodnicka, J. Poltowicz, F. Sanchez, J. Mol. Catal. 109 (1996) 91.
[24] P. Mastrorilli, C.F. Nobile, J. Mol. Catal. 94 (1994) 19.
[25] P. Mastrorilli, C.F. Nobile, Tetrahedron Lett. 35 (1994) 4193.
[26] R. Giannandrea, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. 99 (1994) 27.
[27] P. Mastrorilli, C.F. Nobile, G.P. Suranna, L. Lopez, Tetrahedron 51 (1995) 7943.
[28] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A 108 (1996) 57.
[29] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, L. Lopez, J. Mol. Catal. A 111 (1996) 33.
[30] K. Kaneda, S. Haruna, T. Imanaka, K. Kawamoto, J. Chem. Soc. Chem. Commun. (1990) 1467.

[31] W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, J.S. Valentine, Inorg. Chem. 35 (1996) 1045.

[32] S.I. Murahashi, T. Saito, T. Naota, H. Kumobayashi, S. Akutagawa, Tetrahedron Lett. 32 (1991) 5991.

[33] K. Kaneda, S. Haruna, T. Imanaka, M. Hamamoto, Tetrahedron Lett. 33 (1992) 6827.

[34] C. Bolm, G. Schlingloff, K. Weickhardt, Tetrahedron Lett. 34 (1993) 3405.

[35] K. Kaneda, S. Ueno, T. Imanaka, E. Shimotsuma, Y. Nishiyama, Y. Ishii, J. Org. Chem. 59 (1994) 2915.

[36] N. Mizuno, H. Weiner, R.G. Finke, J. Mol. Catal. 114 (1996) 15.

[37] B. Bhatia, T. Punniyamurthy, J. Iqbal, J. Org. Chem. 58 (1993) 5518.