Tetrahedron Letters, Vol. 34, No. 7, pp. 1123-1126, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Epoxidation of Olefins by Molecular Oxygen with Clay-Impregnated Nickel Catalysts

Ezzeddine Bouhlel[b], Pierre Laszlo[a*], Michel Levart, Marie-Thérèse Montaufier, and Girij Pal Singh

[a*] Laboratoire de chimie fine, biomimétique, et aux interfaces, Ecole Polytechnique, 91128 Palaiseau, France
[b] Faculté des Sciences de Monastir, Département Chimie, Route de Kairouan, 5019 Monastir, Tunisie

Key Words : Heterogeneous catalysis - Aerobic oxidation - Oxygen transfer - Mukaiyama procedure

Abstract : *With the supported "clayniac" catalyst, in the presence of i-butyraldehyde as a sacrificial reducer, olefins are epoxidized in good yields by compressed air at room temperature, in a convenient procedure.*

A search is under way for new epoxidation reagents: aromatic peroxy acids such as m-chloroperbenzoic acid (MCPBA) can no longer be used because unsafe in shipping and handling. One recent and efficient alternative is epoxidation of olefins by vanadium oxide (catalyst) and t-butyl hydroperoxide (oxidant) [1,2]. Another recent report showed that trisubstituted and exo-terminal olefins or norbornene analogs are smoothly oxygenated into the corresponding epoxides in high-to-quantitative yields on treatment with an aldehyde (reducer) under an atmospheric pressure of oxygen (oxidant) at room temperature in the presence of a transition metal complex $Ni(dmp)_2$ as the catalyst [3]. We decided to test a variant of this Mukaiyama procedure: the oxidizing prowess of some natural clays [4], our prior experience with "claynick" [5,6] and the convenience of a supported catalyst [7,8] all made us opt for clay-impregnated nickel acetylacetonate as the catalyst. The choice of nickel (II) as a catalyst for an oxidation reaction has few precedents[10], apart from the $Ni(II)Br_2$—catalyzed oxidation of primary and secondary alcohols to carbonyls by benzoyl peroxide[11] and, more generally, oxidation of organic compounds by "nickel peroxide"[12].

"Clayniac": a solution of nickel acetylacetonate (2g in 20mL of acetone, ca. 0.4M) is stirred under moderate heating (50°C). The K10 montmorillonite (Süd-Chemie; 2g) is then added to the suspension. The solvent is evaporated under reduced pressure, on a rotary evaporator. After careful washing with methylene chloride, to remove non-impregnated nickel, the residue is dried in an atmospheric oven at 100°C overnight.

Standard procedure: a mixture of the olefin (5mmol), the catalyst (50mg), and i-butyraldehyde (1mL: 11mmol) in methylene chloride (10 mL) was stirred at room temperature in an autoclave under 10 bars of compressed air. After completion or interruption of the reaction, the solid catalyst was filtered through a short plug of silicagel. The i-butyric acid formed is removed by washing with an aqueous HCO_3Na solution. The excess of unreacted i-butyraldehyde is evaporated under vacuum together with the solvent. The products were analyzed by GC, by comparison with authentic samples (Aldrich; Janssen) and a n-tetradecane standard was used to determine the yield. Isolated yields are often significantly smaller than the GC yields given in the Tables : secondary products of high molecular weights, polyperoxides presumably[13], stay undetected on the column. Some results are shown in Table 1.

Table 1. Catalyzed aerobic epoxidation of olefins.

Entry	Olefin	Conversion %	Yield, %		Note
1	2,3-dimethyl-2-butene	90	50[a,d]		
2	1-hexene	61	53[a,c]		
3	2-methyl-1-pentene	98	67[a]		
4	2,3,3-trimethyl-1-butene	100	92[a,d]		
5	1-octene	57	29[a,c]		
6	2-methyl-1-heptene	100	67[a]		
7	2,4,4-trimethyl-1-pentene	95	81[a,e]		
8	2,4,4-trimethyl-2-pentene	100	76[a]		
9	1,3,5-trimethyl-1-cyclohexene (*cis* + *trans*)	97	67[a]	50[b,d,e]	4 isomers [d]
10	2-methyl-1-undecene	100	83[a]	45[b,e]	
11	cyclopentene	89	34[a,c]		
12	cyclohexene	97	71[a,c]		
13	cycloheptene	100	89[a]		
14	1-methylcyclohexene	100	87[a]		
15	*cis* cyclooctene	100	100[a,c]		
16	cyclododecene (*cis* + *trans*)	94	80[a]	78[b,e]	2 isomers [e]
17	1,5,9-cyclododecatriene	99	43[a]	33[b,d,e]	2 monoepoxides [d]
	trans-trans-cis			50[b,d,e]	4 diepoxides [d]
18	4-vinylcyclohexene	90	85[a]	60[b,e]	4-vinylcyclohexane oxides : 2 isomers[e]
19	*trans* stilbene	100	95*	92[b,d,e]	*trans* oxide [c,d,e]
20	norbornene	100	74[a,c]		
21	5-norbonene-2-methanol (*endo/exo*)	96	78[a]	60[b,e]	2 isomers [e]
22	(+)-limonene	92	75[a,e]	75[a,e]	2 isomers 1.8 : 1 [a]

* on the column, decomposes partly into 2,2-diphenyl-1-ethanal

[a] determined by GC analysis

[b] isolated yield

[c] retention time by GC analysis identical to that of an authentic sample

[d] identifed by GC/MS

[e] identified by ^{1}H and ^{13}C NMR spectra

Besides the operational ease, this procedure commends itself by its low cost, compressed air serving as the oxidant. The catalyst is prepared from an inexpensive, commercial nickel complex. After the catalyst has been washed thoroughly, there is no leaching of nickel into the solution. Control experiments prove true heterogeneous catalysis to then occur. The catalytic turnovers (greater than 10^5 for a 99.2% yield of cyclooctene oxide, and than $2 \cdot 10^6$ for a 82% yield of the same oxide) are gratifying. The reproducibility is also satisfactory, with yields invariant to ± 5%. The wide margin between conversion and yield with volatile olefins such as 1-hexene, cyclohexene, cyclopentene, etc. stems from evaporation of the olefin while the autoclave is depressurized. Polymerization of the olefins is another source of loss on some substrates. As a rule nevertheless, the selectivity is excellent. With this methodology, little or no allylic oxidation into the alcohol or the α,β-unsaturated ketone occurs. Neither does isomerization take place: the terminal olefins 1-hexene and 1-octene do not turn into 2-hexene or 2-octene. Comparison with other literature methods is to the advantage of this montmorillonite-based variant to the new Mukaiyama procedure[3]. Various other methods give lower yields and/or allylic oxidation in the epoxidation of cyclohexene as the test substate[14-17]. While the best results are obtained in methylene chloride, a more environment-friendly non-chlorinated solvent such as t-butanol (Table 2) or methyl t-butyl ether can also be used, at least with the more activated olefins such as cyclooctene.

Table 2. Epoxidation in t-butanol under 30 bars of air.

Olefin	Reaction time/h	Conversion %	Yield % [c],[d]
1-Hexene	16	98	40
Cyclohexene	16[a]	93	31 + 3[b]
1-Me-Cyclohexene	16[a]	100	83
Cyclopentene	16	60	12
Cycloheptene	4	67	36
cis Cyclooctene	4	85	65
Norbornene	3	95	63
Styrene	16	91	11
(+)-Limonene	4	93	67
α-Pinene	16	100	26
β-Pinene	16	95	10

[a] 10 bar air pressure
[b] ketone from allylic oxidation
[c] determined by GC analysis
[d] GC retention time identical to that of an authentic sample

Longer reaction times, typically 16 h, are required. With a dozen test olefins, the yields in t-butanol under 30 bars of air are lower than in methylene chloride by 20-30%. More generally, sluggish reactions show improved conversions or yields by raising the air pressure, or by resorting to pure oxygen.

This methodology, while commendable for its simplicity, has some drawbacks. It is not applicable to unreactive olefins. Yields are not quantitative. One has to invest stoichiometric amounts of i-butyraldehyde as a sacrificial reducer, whose role is that of an oxygen transfer agent. The likely mechanism is co-oxidation of the sacrificial aldehyde and the olefin. The aldehyde is converted by dioxygen into, first the acyl, second the acylperoxy radical. The olefin is epoxidized either by the acylperoxy radical or by the corresponding peracid produced in situ[18-21]. The influence of the nature of the aldehyde on the ease of the epoxidation is examined in the accompanying communication. With i-butyraldehyde, the resulting i-butyric acid has to be separated from the epoxide product, which detracts from the usefulness of the methodology. A one-electron oxidation process appears excluded, by the lack of a correlation between the observed reactivities (cf. Table 1) and the half-wave oxidation potentials of the olefins from the literature[22-23]. Accordingly, we are working on ways to circumvent these minor blemishes, trying a co-catalyst for instance. Nevertheless, as also shown by others recently[24], the Mukaiyama procedure[3] can be adapted to good use.

Acknowledgements

This work was supported by the award of postdoctoral fellowships to EB by L'Oréal and to GPS by the Ecole Polytechnique. We have benefited also from support by Ministère de la Recherche et de la Technologie (contrat No. 89T0296).

References

1 - Laszlo, P. ; Levart, M. ; Singh, G.P., *Tetrahedron Lett.*, **1991**, *32*, 3167-3168.

2 - One reason to seek other epoxidation catalysts is the possible long-term toxicity of inhaled vanadium pentoxide particles ; they undergo one-electron redox cycling in rat lung biomembranes. Reoxidation of V(IV) initiates lipid peroxidation under aerobic conditions : the analogy with cytochrome-P450, that initiated our work, is indeed compelling. Zychlinski, L. ; Byckzowski, J. Z. ; Kulkarni, A.P. ; *Arch. Environ. Contam. Toxicol* **1991**, *20*, 295-298.

3 - Yamada, T. ; Takai, T. ; Rhode, O. ; Mukaiyama, T., *Chem. Lett.*, **1991**, 1-4 ; *Bull. Chem. Soc. Jpn*, **1991**, *64*, 2109-2117. Mukaiyamza, T. ; Takai, T. ; Yamada, T. ; Rhode, O., *Chem Lett.*, **1990**, 1661-1664.

4 - There exist in Brazil red earths produced by laterization having 5 meq.$(100g)^{-1}$ Fe^{3+}. These minerals are such strong oxidants that workers digging trenches in Amazonia were suffocated by the carbon dioxide produced as soon (5-10 mn) as the organic matter of the humus came into contact with air in the presence of the underlying clay : Persio de Souza Santos, *Ciência e Tecnologia de Argilas*, 2nd ed., Edgard Blücher, Sao Paulo, SP, Brazil **1989** ; and personal communication to PL, August **1989**.

5 - K10 montmorillonite (Süd-Chemie, München) impregnated with Ni(II).

6 - In conjunction with ferric chloride, it catalyzes the Michael reaction : Laszlo, P. ; Montaufier, M.T. ; Randriamahefa, S.L , *Tetrahedron Lett.*, **1990**, *31*, 4867.

7 - There is little or no contamination of organic products or solvents by inorganic materials. After repeated washing of the fresh supported catalyst by methylene chloride, followed by the epoxidation procedure, only traces of nickel are found in the solvent. Product isolation involves only decantation or filtration, followed by evaporation of the solvent.

8 - Laszlo, P., (Ed.) : *Preparative Chemistry Using Supported Reagents*, Academic Press, San Diego, CA, USA 1987, 2 vols.

9 - Laszlo, P., "Solid-supported Oxidants", in *Comprehensive Organic Synthesis* - Vol. 7 *Oxidation*, Ley, S.V. (Ed.), Pergamon Press, Oxford, 1991, pp. 839-848.

10 - Haines, A.H., *Methods for the Oxidation of Organic Compounds*, Alkanes, Alkenes, Alkynes, and Arenes, Academic Press, London, 1985.

11 - Doyle, M.P. ; Patrie, W.J. ; Williams, S.B., *J. Org. Chem.*, **1979**, *44*, 2955-2956.

12 - Mijs, W.J. ; De Jonge, C.R.H.I. ; (Eds), *Organic Syntheses by Oxidation with Metal Compounds*, Plenum Press, New York, 1986, ch. 6, pp. 373-422.

13 - Emanuel N.M., Zaikov G.E., and Maizus Z.K., *Oxidation of Organic Compounds*, Pergamon Press : Oxford, 1984, pp. 46-67.

14 - Groves J.T., Nemo T.E., *J.Am.Chem.Soc.*, **1983**, *105*, 5786-5791.

15 - Smegal J.A., Hill C.L., *J.Am.Chem.Soc.*, **1983**, *105*, 2920-2922.

16 - Kuroda Y., Hiroshige T., Ogoshi H., *J.Chem.Soc. Chem. Comm.*, **1990**, 1594-1595.

17 - Brill W.F., Indictor N., *J. Org. Chem.*, **1963**, *29*, 710-713.

18 - Tsuchiya, F. and Ikawa, T., *Can. J. Chem.*, **1969**, *47*, 3191-3197.

19 - Vreugdenhil, A.D. and Reit, H., *Rec. Trav. Chim. PB*, **1972**, *91*, 237-245.

20 - Haber, J.; Mlodnicka, T. and Poltowicz, J., *J. Mol. Catal.*, 1989, 54, 451-461.

21 - Iwanejka, R. ; Leduc, P. ; Mlodnicka, T. and Poltowicz, J., in *Dioxygen Activation and Homogeneous Catalytic Oxidation*, L.I. Simandi, Ed., Elsevier, Amsterdam, 1991.

22 - Bauld N.L., *Tetrahedron*, **1989**, *45*, 5307-5363.

23 - Garrison J.M., Ostovic D., Bruice T.C., *J.Am. Chem. Soc.*, **1989**, *111*, 4960-4966.

24 - Irie R., Ito Y., Katsuki T., *Tetrahedron Lett.*, **1991**, *32*, 6891-6894.

(Received in France 8 October 1992)