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Journal of Molecular Catalysis A: Chemical 108 (1996) 15–21

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Terpenic olefin epoxidation using metals acetylacetonates as catalysts

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Received 29 May 1995; accepted 16 October 1995

Abstract

Efficient epoxidation of natural terpenic olefins is performed using nickel acetylacetonate, oxygen and a branched aldehyde at ambient temperature. Total conversions are achieved with selectivities up to 90% into epoxide. Under the same conditions other catalytic systems using transition metal acetylacetonates ($M^n(acac)_n$) have been used, some of which also gave satisfactory results.

Keywords: Epoxidation; Nickel; Acetylacetonate; Transition metals; Terpenic olefins; Oxygen

1. Introduction

Essential oils of pine trees that generally contain more than 80% of terpenic olefins, is an extremely useful source of starting material for several high value industrial processes used for the synthesis of fragrances and pharmaceutical compounds.

A new route to high added value compounds from these natural products is therefore a challenge, among which catalytic functionalization of olefins is probably of major interest. In particular, the olefin epoxidation catalyzed by transition metal salts [V, Mo, Fe, Ti, etc.] in the presence of an oxidant (H_2O_2, tBuOOH, peracids, PhIO, etc.) has been performed selectively and sometimes with a high degree of enantioselectivity.

Recently, Mukaiyama et al. [1] have described a very simple catalytic combination [$Ni(acac)_2/RCHO/O_2$) which allows the synthesis of epoxide under mild conditions (1 atm O_2, ambient temperature). The ligand structure (1,3 diketones) and that of the aldehyde have been studied, in an effort to determine the best catalytic combination in terms of activity and selectivity [1,2]. Other transition metal based catalysts have also been reported to exhibit high activities for cyclic olefins epoxidation (Ni supported catalyst [3], Ru salts [4] cobalt Schiff's base complexes [5]).

In connection with our on going interest in catalytic functionalization of terpenic olefins [6],

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SSDI 1381-1169(95)00284-7

we report here some data obtained in their epoxidation under oxygen using metal acetylacetonates complexes and isobutyraldehyde as reductant.

2. Results and discussion

The olefins are epoxidized in a 1,2-dichloroethane solution of isobutyraldehyde and the catalytic complex $[M^n(acac)_n]$, by a continuous bubbling of molecular dioxygen.

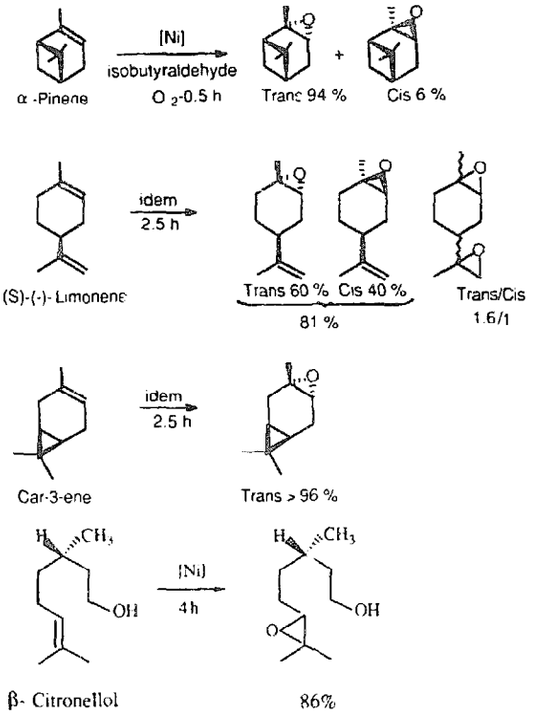
Samples of catalytic solution are taken from time to time and analyzed by GC.

2.1. Epoxidation of different terpenic olefins

Various terpenic olefins have been epoxidized in an effort to look at the chemo- and stereoselectivity of these reactions, using nickel(II) acetylacetonate as standard catalyst (see Table 1).

Upon using (+)-α-pinene as substrate (Scheme 1) a total conversion is observed within 30 min, with a 93% selectivity into epoxide; both stereoisomers (*cis* and *trans*) are obtained, in a 94/6 ratio. The major isomer is the *trans* form, as deduced from high field NMR studies [7].

With (*S*)-(−)-limomene, again a 100% conversion is obtained with a chemoselectivity into monoepoxide of 81% (*trans*/*cis* = 60/40) [4].



Scheme 1. Epoxidation of different monoterpenes.

As determined by GC–MS spectroscopy, some diepoxidation was also observed (17%) with predominantly the *trans* isomer (*trans*/*cis* = 1.6/1).

(+)-Car-3-ene is much less reactive than the above isomers, as a 97% conversion is only reached after 5 h. The *trans* isomer is only obtained; its stereochemistry (see Scheme 1) was determined after purification and NMR

Table 1
Catalytic epoxidation of monoterpenes [a]

No.	Substrate	Reaction time (h)	Conversion (%)	Epoxide selectivities (%)	*trans*/*cis*
1	(+)-α-pinene	0.5	100	93	94/6
2	(*S*)-(−)-limonene	2.5	100	81 [b]	60/40
3	(+)-car-3-ene	2.5	97	90	96/4
4	(+)-car-2-ene	5	96	89	100/0
5	(+)-*p*-menth-1-ene	1.5	90	90	60/40
6	(+)-*trans*-isolimonene	6	100	91	100/0
7	(*S*)-β-citronellol	4	90	86	– [c]
8	(*R*)-(−)-carvone	36	100	70	

[a] Conditions: 1,2-dichloroethane = 5 ml, $Ni(acac)_2$ = 0.16 mmol, isobutyraldehyde = 24 mmol, olefin = 8 mmol. Conversions and selectivities were determined by GC.

[b] A further epoxidation of the external double bond was observed (see text).

[c] Diastereoisomeric ratio: 50/50.

analyses from a comparison of the latter with literature data using the chemical shift difference between the gem dimethyl groups [7].

The internal double bond of (+)-menth-1-ene reacts with a 90% selectivity to gives the corresponding epoxide with a 60/40 *trans/cis* ratio similar to that observed with limonene, whereas (+)-*trans*-isolimonene arising from the isomerisation of (+)-car-2-ene [8] gives a conversion of 100% in 6 h with a 91% selectivity.

Finally (*R*)-(−)-carvone, which presents the same structure as limonene but with a carbonyl group in an α position to the endocyclic double bond has very poor reactivity, as 36 h are necessary for the reaction to go to completion.

2.2. Catalytic system: role of the metal and of the ligand

Nobile et al. have achieved the efficient epoxidation of cyclic olefins with β-ketoesterate complexes of iron(III), nickel(II) and cobalt(II) [2]. Epoxidation of some terpenic olefins have also been reported with cobalt(II) Schiff's base complexes [5] and with supported nickel catalyst [3].

Attempts carry out the epoxidation of (+)-α-pinene have been made in an effort to see whether this catalytic reaction could be performed efficiently with other transition metal acetylacetonates (Table 2).

Cu, Cr, Pd and Rh acetylacetonates are almost inactive, whereas Mo, V and Zr complexes show moderate activities and epoxide selectivities. It is clear that first row transition metal elements are much more suitable, particularly cobalt, manganese and nickel.

Furthermore, to determine whether acetylacetonate ligands play a role during the epoxidation elementary step, we have synthesized chiral β-diketones from camphor according to a procedure already described by Togni [9] and the corresponding nickel and manganese complexes (Scheme 2).

These complexes have been tested in the epoxidation of (*S*)-(−)-limomene and β-citronellol, this last substrate gives diastereoisomers easily separated by GC (Scheme 1).

Table 2
Catalytic epoxidation of (+)-α-pinene on different acetylacetonate complexes [a]

Catalyst	Reaction time (h)	Conversion (%)	Epoxide selectivity (%)
$Cu(acac)_2$	5	0	–
$Cr(acac)_3$	8	0	–
$Rh(acac)_3$	6	0	–
$Pd(acac)_2$	7	12	0
$Zr(acac)_4$	5	53	20
$VO(acac)_2$	7	60	21
$MoO_2(acac)_2$	7.5	48	44
$Co(acac)_3$	1	98	93
$Co(acac)_2$	3	97	91
$Fe(acac)_3$	4	99	89
$Mn(acac)_3$	1	100	93
$Ni(acac)_2$	0.5	100	93

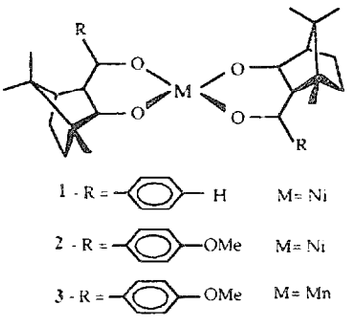
[a] Conditions: same as in Table 1.

As already mentioned by Mukaiyama, substitution of diketonato ligand by electrodonating groups enhances the activity. But with limonene the *cis/trans* ratio of mono or diepoxide obtained with complexes **1**, **2** and **3** is almost the same as that observed in experiments carried out with $Ni(acac)_2$.

In the same way Table 3 shows that the epoxidation of β-citronellol leads to an enantiomeric excess close to zero whatever the ligand or metal used.

2.3. Mechanistic considerations

Although it is difficult to delineate a detailed catalytic cycle with certainty, upon analysis of



Scheme 2. (+)-Bis(3-benzoylcamphorato) and (+)-bis[(*p*-methoxy)benzoylcamphorato]nickel and manganese complexes.

Table 3
Epoxidation of (*S*)-β-citronellol catalyzed by different β-diketone complexes [a]

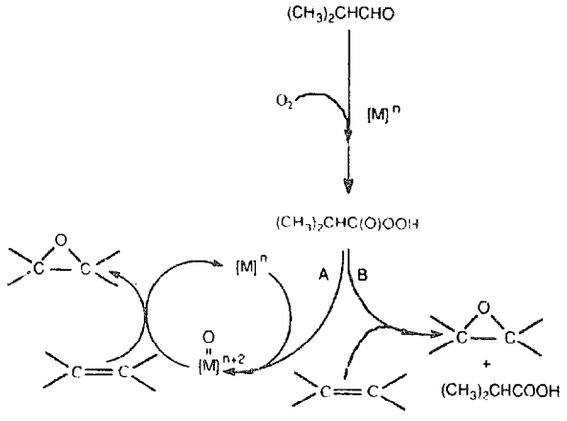
Catalyst	Time (h)	Conversion %	Epoxide selectivity %	ee [b] (%)
1	3	95	90	0.1
2	2	96	90	0.6
3	2	96	90	0.5

[a] Conditions: 1,2-dichloroethane = 3 ml, catalyst = $6.7.10^{-2}$ mmol, isobutyraldehyde = 9 mmol, (*S*)-β-citronellol = 3 mmol.
[b] ee: enantiomeric excess, determined by GC analysis (β-cyclodex column).

above experiments and from the literature [1,10,11] a plausible mechanism can be proposed (Scheme 3), in which the first step can be the oxidation of aldehyde into peracid. At ambient temperature (20–25°C) this oxidation does not occur in the absence of metallic catalyst. However at higher temperature (up to 45–50°C) the formation of peracid and therefore subsequent epoxidation of olefin is observed without catalyst, as recently reported with other olefins [12].

This fact suggests that epoxidation occurs by reaction of peracid initially formed with the olefin according to the Prilezaev reaction [13]. For this step two different pathways (A and B, Scheme 3) can be proposed:

(i) In path A the Prilezaev reaction is catalysed by a transition metal moiety. In this process the peracid reacts with a metallic species to give an oxometalate complex which oxidizes the olefin into epoxide [14] and regenerates the initial catalytic species.



Scheme 3. proposed mechanism for epoxidation of terpenic olefins.

(ii) The peracid can also directly react with the olefin to produce the epoxide (path B).

The observation that chiral ligands have practically no influence on the stereoselectivity of the reaction, could indicate that path B in which the chiral catalytic complex does not intervene in the last step of the epoxidation, is the most probable. However, it is also conceivable that the chiral ligands are not able to give asymmetric induction [1].

3. Conclusion

The functionalization of different natural terpenic olefins such as α-pinene, limonene, etc. into the corresponding epoxide can be carried out under very mild conditions and in high yield by using a simple catalytic system consisting of a transition metal complex (Ni, Fe, Co, Mn) with β-diketono ligands, branched aldehyde and molecular oxygen. Unfortunately, the replacement of classical acetylacetonate by chiral β-diketones derived from camphor did not result in the enantioselective epoxidation of prochiral olefins.

4. Experimental

The ^{1}H (300 or 400 MHz) and ^{13}C (75.45 MHz) spectra were recorded on Bruker AC 300

[1] In order to verify these assumptions, isobutyraldehyde (24 mmol) in a solution in dichloroethane (15 ml) was oxidized in the absence of metallic catalyst by heating at 55°C for 3 h. Then the mixture was cooled at ambient temperature and α-pinene (8 mmol) was added. Analyses of the periodic samples have shown that α-pinene was efficiently epoxidized in these conditions whereas, as already mentioned, there is no reaction without initial heating. However the rate of epoxidation under these conditions was much lower (25 and 52% conversion for $t = 1$ and 5 h, respectively) than that observed with metal catalyst (see Table 1, entry 1). Therefore it is also possible that the two pathways A and B occur simultaneously.

or AM 400 spectrometers, using $CDCl_3$ as solvent, chemicals shifts are given in ppm relative to external TMS and coupling constants (J) in Hz. Gas chromatographic analyses were performed on a Delsi 3000 or a Chrompack 9001 gas chromatograph using fused silica capillary columns (CP-Sil 5CB column (Chrompack): 25 m × 0.32 mm for general separations or FS Cyclodex β 25 m × 0.32 mm for separations of β-citronellol epoxides). A DB1 30 m × 0.25 mm column was used for GC–mass coupled analyses with a ConceptII spectrometer (Kratos Analytical Ltd). Merck silica gel 60 (70–230 mesh) and basic aluminium oxide (50–200 μm) were used for flash column chromatography.

4.1. Products

All reactants and solvents were purchased from Janssen Chimica or Aldrich and were used without further purification, except for (+)-*trans* isolimonene which was synthesized according to [8].

4.2. Preparation of chiral camphor derivatives

3-Benzoylcamphor was synthesized according to [9], (*p*-methoxy)-3-benzoylcamphor was obtained by an adapted procedure described in the same reference from 10 g (65.5 mmol) of (+)-camphor, 3.7 g (0.154 mol) of NaH in 100 ml of DMF and 11.93 g (72.2 mmol) of methyl *p*-methoxybenzoate in 40 ml of DMF; yield 80%.

^{1}H NMR ($CDCl_3$): δ 0.99 (s; 3H), 1.1 (s; 3H), 1.15 (s; 3H), 1.3–1.8 (m; 4H), 2.5 (t; J = 4.2; 1H), 3.8 (s; 3H), 4.2 (d; J = 4.6; 1H), 7.05 (m; 2H), 7.6–7.9 (m; 3H). ^{13}C NMR ($CDCl_3$): δ 9.6 (q), 18.8 (q), 19.6(q), 20.2(t), 27.8(t), 46.3(s), 48.53(d), 57.5(q), 58.5(s), 58.7(d), 113.8(d), 130(d), 195.7(s), 213.2(s).

4.3. Preparation of complexes 1, 2, 3

4.3.1. Complex 1

To 4.6 g (18.2 mmol) of 3-benzoylcamphor dissolved in 60 ml of diethyl ether was added a solution of 2.26 g (9.1 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ in 160 ml of an ammoniacal solution (10% $NH_4(OH)$). After stirring for 0.5 h the green precipitate was filtered off, washed with a small amount of cold water and dried in vacuo; yield 4.8 g (90%).

$[\alpha]_D^{20} = +177$ (C = 1, $CHCl_3$). Anal. Calcd for $(C_{34}H_{38}O_4)Ni$: C, 71.74; H, 6.68; O, 11.25 Found: C, 70.98; H, 6.68; O, 11.71.

4.3.2. Complex 2:

Complex 2 was obtained similarly.

$[\alpha]_D^{20} = +227$ (C = 1, $CHCl_3$). Anal. Calcd for $(C_{36}H_{42}O_6)Ni$: C, 68.71; H, 6.68; O, 15.26 Found; C, 70.00; H, 7.49; O, 16.32.

4.3.3. Complex 3

To a solution of 0.44 g (3.5 mmol) of $MnCl_2$ in 15 ml of water was added 2 g (7 mmol) of (*p*-methoxy)-3-benzoylcamphor in 15 ml of MeOH. The mixture was stirred and 0.95 g of NaOAc dissolved in 15 ml of water and 5 ml of a concentrated solution of NH_4OH are successively added and stirring was continued for 15 min. The mixture was then cooled to 4°C during several hours. The product precipitated as microcrystalline material which was filtered off, washed with cold water and dried in vacuo; yield 2.15 g (91%). $[\alpha]_D^{20} = +92$ (C = 0.1, $CHCl_3$). Anal. Calcd for $(C_{36}H_{42}O_6)Mn \cdot 2H_2O$: C, 65.36; H, 6.95; O, 19.30 Found: C, 65.63; H, 6.79; O, 19.08.

4.4. General procedure for olefin epoxidation

In a typical experiment, 0.16 mmol of $M^n(acac)_n$ and 24 mmol of isobutyraldehyde were dissolved in 5 ml of 1,2 dichloromethane and introduced in a round bottom flask equipped with a gas bubbler and a condenser. Oxygen was gently bubbled into the solution, the olefin (8 mmol) was added to the medium and the mixture was stirred at ambient temperature. Aliquot samples were taken at regular intervals and analysed by GC. At the end of the reaction, the solvent was evaporated and the residue was

chromatographed on a short column of basic alumina with hexane/ethyl acetate (9/1 v/v) as eluent, in order to neutralise the isobutyric acid formed during the reaction and separate the catalyst. The epoxides were then purified by flash chromatography on silica gel with the same eluent.

In the case of the epoxidation of car-2-ene and β-citronellol, the neutralisation was carried out by stirring the reaction mixture with a solution of $NaHCO_3$ up to pH 8–9. The organic layer was dried over Na_2SO_4, the solvent was evaporated and the epoxide purified as above.

4.4.1. Characteristics of the epoxides

Epoxide of (+)-α-pinene:

^{1}H NMR ($CDCl_3$): δ 3.04(dd; J = 4.1, 1.1, 1H), 1.96 (m; 2H), 1.92 (m; 1H), 1.90 (m; 1H), 1.70 (m; 1H), 1.59 (d; J = 9.4; 1H), 1.32 (s; 3H), 1.26 (s; 3H), 0.91 (s; 3H). ^{13}C NMR ($CDCl_3$): δ 60.2(s), 56.7(d), 44.9(d), 40.4(s), 39.6(d), 27.5(t), 26.6(q), 25.8(t), 22.3(q), 20.1(q).

4.4.2. Epoxides of (S)-(−)-limomene

Monoepoxide (mixture of *cis/trans* epoxides):

^{1}H NMR ($CDCl_3$): δ 4.67 (s; 1H), 4.61 (s, 1H), 3 (m; 1H (*trans*)), 2.98 (d; J = 5; 1H (*cis*)), 2.1 (m; 1H), 1.85 (m; 2H), 1.65 (m; 2H), 1.6 (m;2H), 1.25 (s; 3H), 1.2 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.93(s), 109.03(t), 59.25(d), 57.35(s), 40.68(d), 30.67(t), 28.56(t), 25.85(t), 23.07(q), 20.19(q).

4.4.3. Diepoxide

^{1}H NMR ($CDCl_3$): δ 3.02 (m; 1H), 2.5(m; 2H), 2.15 (m; 1H), 1.8 (m; 2H), 1.6 (m; 2H), 1.55 (m; 2H), 1.25 (s; 3H), 1.20 (s; 3H). ^{13}C NMR ($CDCl_3$): δ 60.04(d), 52.64(t), 34.79(d), 28.41(t), 27.69(t), 24.29(q), 23.56(t), 18.77(q). MS m/z 168 (M^+), 43.

4.4.4. Epoxide of car-3-ene

^{1}H NMR ($CDCl_3$): δ 2.77 (s; 1H), 2.24 (m; 1H), 2.08 (dd; J = 8.9, 7.2; 1H), 1.55 (m; 2H), 1.2 (s; 3H), 0.95 (s; 3H), 0.67 (s; 3H), 0.5 (m; 2H). ^{13}C NMR ($CDCl_3$): δ 58.17(d), 55.9(s), 27.7(q), 23.2(t), 23.0(q), 19.1(t), 15.9(d), 14.5(q), 13.7(d).

4.4.5. Epoxide of car-2-ene

^{1}H NMR ($CDCl_3$): δ 2.9 (s; 1H), 1.6–1.9 (m; 4H), 1.35 (s; 3H), 1.25 (m; 1H), 1.15 (s; 3H), 1.1 (s; 3H), 0.8 (m;1H). ^{13}C NMR ($CDCl_3$): δ 58.3(s), 57.8(d), 28.8(q), 27.4(t), 23.6(q), 21.7(d), 20.9(t), 20.6(s), 17.4(q), 16.4(d).

4.4.6. Epoxide of (+)-menth-1-ene

^{1}H NMR ($CDCl_3$): δ 2.89 (m;1H), 2.0 (m; 1H), 1.85 (m; 1H), 1.65 (m; 2H), 1.5 (m; 2H), 1.4 (m; 2H), 1.3 (s; 3H), 0.92 (s; 3H), 0.91 (s; 3H). ^{13}C NMR ($CDCl_3$): δ 59.5(d), 57.7(s), 35.0(d), 31.5(d), 29.0(t), 27.7(t), 24.3(q), 23.0 (q), 22.4(t), 19.6(q).

4.4.7. Epoxide of citronellol

^{1}H NMR ($CDCl_3$): δ 3.4 (m; 2H), 2.55 (t; 1H), 1.5–1.2 (m; 7H), 1.14 (s; 3H), 1.10 (s; 3H), 0.7 (d; 3H).

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