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Co(II) Catalysed Oxidation of α-Pinene by Molecular Oxygen. Part 2

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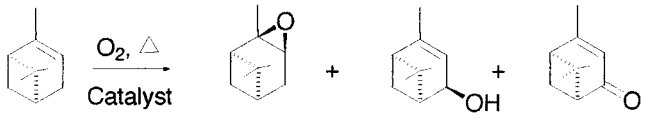
Abstract—This paper reports studies of factors affecting air oxidation of (−)-α-pinene catalysed by Co(II)–pyridine complexes without a concomitant co-oxidant. Observations are presented about the nature and amount of the catalyst, reaction temperature, oxygen flow and solvent vs. non-solvent conditions. In addition, attention has been paid to the influence of added base or acid, and identification of side products. © 2000 Elsevier Science Ltd. All rights reserved.

Aerobic oxidation of organic olefinic substrates catalysed by various metal complexes in the presence of alcohols, aldehydes, ketones, ketoesters or acetals has recently been the subject of several papers.[1] Less attention has been paid to catalytic air oxidation of olefins without co-oxidant.[2] We have reported a facile method to prepare verbenone (**1**) in high yield by air oxidation of (−)-α-pinene (**2**) catalysed by Co(II) complexes under solvent free conditions.[3] Liquid-phase auto-oxidation of olefins is a radical chain process



2 **3** **4** **1**

and the chain propagation can occur via the usual abstraction mechanism to produce allylic oxidation products or via the addition of alkylperoxy radical to the double bond, followed by unimolecular decomposition to give an epoxide.[4] Herein we report our observations concerning the nature and the amount of catalyst, the reaction temperature and the oxygen flow rate. Additionally, attention was paid to solvent vs. non-solvent conditions, and the effect of added base or acid.

Results and Discussion

Catalyst

First we investigated the nature of the Co(II) catalyst. The best results for air oxidation of α-pinene were obtained by using [Co(4-methylpyridine)$_2$Br$_2$] as the catalyst.[3] However, the unsubstituted analog [Co(pyridine)$_2$Br$_2$] was chosen for comparison to gain further insight into the effect of the catalyst. Concurrent air oxidations of α-pinene at 60°C were performed by using $CoBr_2$, $CoBr_2{\cdot}H_2O$, [Co(pyridine)$_2$Br$_2$] and weighed amounts of components needed for the formation of the complex, $CoBr_2{\cdot}H_2O$ and pyridine. In addition, a sample without a catalyst was included in the air oxidation, but no oxidation was detected after 30 h. Air oxidations in which the catalyst was a ready-made complex or where it was generated in situ, proceeded equally well, producing 27% of verbenone in 23 h. Anhydrous $CoBr_2$ and $CoBr_2{\cdot}H_2O$ were ineffective as catalysts.

The amount of catalyst used in our air oxidations of α-pinene varied from 0.1 to 0.5 mol%, though usually it was 0.15 mol%. The effect of the amount on air oxidation was studied by using 7.5, 1.5, 0.15 and 0.05 mol% of [Co(4-methylpyridine)$_2$Br$_2$]. The reaction with the two lowest amounts of the catalyst started and proceeded with equal success. Air oxidations with the largest amounts of the catalyst (1.5 or 7.5 mol%) were slower and produced less verbenone than the reactions with less catalyst (Fig. 1).

In conclusion, pyridine has an essential role in the active catalyst species, which can also be generated during the air oxidation. The catalyst amount 0.05 mol% is sufficient to catalyse air oxidation.

Reaction temperature

We have reported that an increase of reaction temperature with the same catalyst accelerated air oxidation of α-pinene.[3] However, completion of α-pinene air oxidation

Keywords: air oxidation; Co(II) catalyst; α-pinene.
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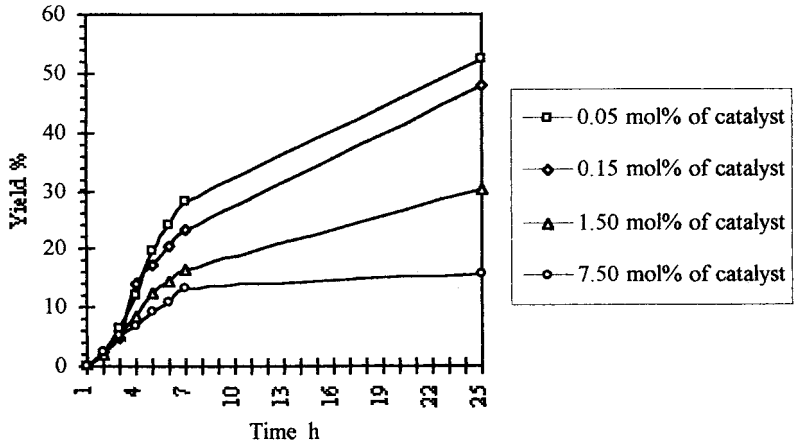


Figure 1. Percentage yield of verbenone as a function of $[Co(4\text{-mepy})_2Br_2]$ catalyst at 100°C.

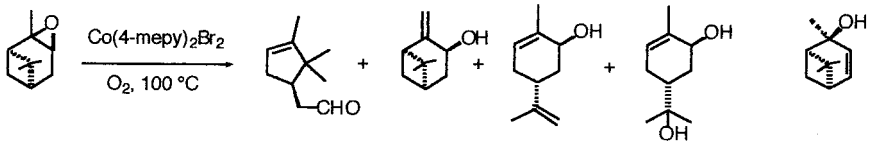
at 50°C took days. Furthermore, we noted that a short heating of a sample of an incomplete air oxidation at 115°C promoted the reaction significantly. To shorten the reaction time air oxidation was performed at 80, 100 and 120°C. At all three temperatures air oxidation commenced quickly by formation of α-pinene oxide (**3**). Next was produced *trans*-verbenol (**4**) and somewhat more slowly verbenone (**1**). The amount of α-pinene oxide reached a maximum in 3 h at 80°C (11%), and in 2 h at both 100°C (8%) and 120 (5%), after which time it began to reduce. For verbenone, the most advantageous reaction temperature was 100°C where in 6.5 h the yield rose to 37%. α-Pinene oxide (**3**) was the intermediate product, but it was absent among the final products. Epoxidation of α-pinene surprisingly produced side products with the same GC retention times as air oxidation of α-pinene. To explain this behaviour (−)-α-pinene oxide (**3**) was air oxidised using $[Co(4\text{-methylpyridine})_2Br_2]$ as a catalyst at 100°C. Rearrangement started immediately and in 6 h 75% of epoxypinane had rearranged, producing 19% of **5**, 19% of **6**, 11% of **7** and 7% of **8** (Scheme 1). Formation of a ring contracted aldehyde under the influence of a Lewis acid is a typical reaction of monoterpene oxides.[5] Comparison of the GC retention times of product mixtures from air oxidation and the rearrangement reaction, showed that numerous minor products formed during air oxidation, resulted from the rearrangement of (−)-α-pinene oxide. The moment when the portion of pinene oxide started to decrease indicates that the rate of rearrangement of epoxide has exceeded that of epoxidation.

Oxygen flow

Earlier we observed that the increase of oxygen flow speeds up air oxidation of α-pinene.[3] The linearity of this effect was studied by performing air oxidation at 100°C using the O_2 flow of 5, 10 and 15 ml/min. The increase in oxygen flow accelerated air oxidation. With the highest flow, α-pinene converted nearly completely in 24 h, producing the highest content of pinene oxide and verbenone (Fig. 2).

Solvent

All our α-pinene air oxidations were performed without a solvent.[3] To see if a solvent would affect the course of air oxidation the reaction was performed in toluene, acetonitrile and dimethylformamide at 60°C. Tetrahydrofuran was excluded because it is known to be autoxidised by cobalt complexes.[2c,6] In the above solvents at 60°C, no air oxidation of (−)-α-pinene using $[Co(4\text{-methylpyridine})_2Br_2]$ as catalyst was detected in 23 h. Under the parallel non-solvent conditions 76% of (−)-α-pinene was converted producing 35% yield of verbenone. A similar retarding influence has also been reported for benzene, chlorobenzene and dichloromethane.[2d] For comparison, air oxidation in acetonitrile was performed at 100°C. Not until after 3 h did the colour of the reaction mixture began to turn greenish, and the first signs of product formation were detected. Only 26% of (−)-α-pinene converted in 24 h producing 9% of verbenone. Bubbling air through the catalyst in acetonitrile (3 h) before



3		5	6	7	8	9
76 %	1 h	9 %	9 %	3 %	3 %	
61 %	3 h	13 %	13 %	5 %	6 %	
25 %	6 h	19 %	19 %	11 %	7 %	

Scheme 1.

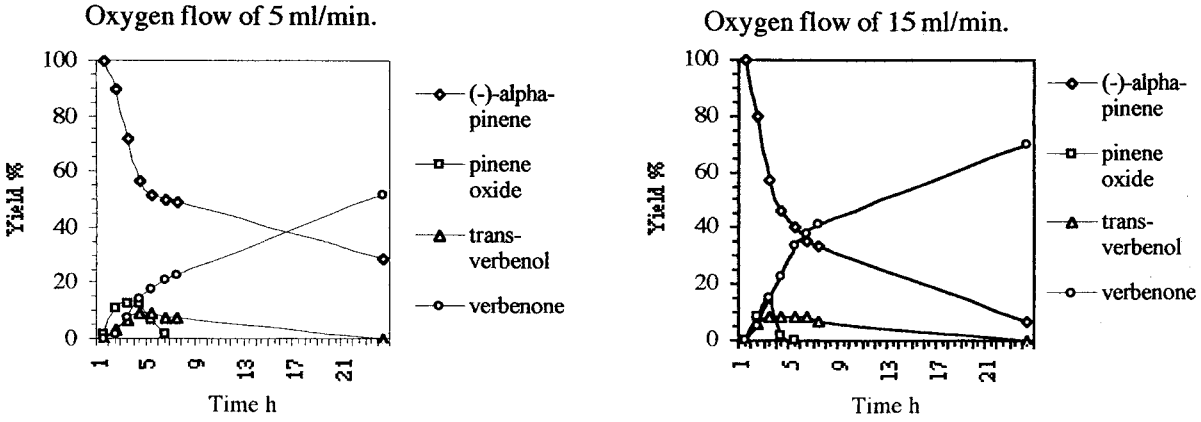


Figure 2. Typical air oxidations of (−)-α-pinene at 100°C.

addition of the substrate did not improve the reactivity. The same reaction by using old peroxidated α-pinene started directly but the progress was no better (10% of verbenone in 24 h).

Effect of added base or acid

Next we were interested in the effect of added base or acid upon the conversion of α-pinene (Table 1). Weighed amounts of $CoBr_2 \cdot H_2O$ and pyridine for the catalyst (0.13 mol%) were added to (−)-α-pinene through which oxygen was bubbled. Pyridine or glacial acetic acid (10 vol%) was apportioned into the reaction mixture and the reaction was held in a 50°C bath. Glacial acetic acid significantly promoted the air oxidation but also speeded up the rearrangement of pinene oxide. Excess pyridine retarded the reactivity of α-pinene and directed air oxidation more toward epoxidation than allylic oxidation. When glacial acetic acid was replaced with trifluoroacetic acid, air oxidation was clearly slower.

The success of glacial acetic acid led us to study its contribution. Air oxidation was carried out by using 2, 5, 10 and 20 vol% of glacial acetic acid (Table 2). A high amount of acid seemed to favour more allylic oxidation than epoxidation but it also resulted in rearrangement of pinene oxide to numerous minor side products (<2%). Mass spectrometric analysis indicated that the product mixture contained some verbenyl acetate when the reaction mixture contained the high amount of acid. Using $Co(AcO)_2$ as a catalyst, instead of the added glacial acetic acid did not improve air oxidation. $Co(AcO)_2$ with pyridine (corresponding to 0.13 mol% of in situ formed catalyst) showed nearly equal catalytic activity to $CoBr_2$ with pyridine in air oxidation.

Side products

All intermediate products had the molecular ion *m/z* 152 and they experienced the loss of M-18.[3] Therefore, they have to be isomeric compounds to verbenol. Four components of intermediate products of α-pinene air oxidation were separated by flash chromatography and were identified as α-pinene oxide (**3**), *trans*-3-pinen-2-ol (**9**), *trans*-verbenol (**4**) and verbenone (**1**). A minor amount (2–6%) of *trans*-3-pinen-2-ol (**9**) formed in the early stages of air oxidation and in pinene oxide rearrangement under catalytic air oxidation conditions. *cis*-Verbenol was excluded by using GC comparison of the product verbenol with *cis*-verbenol obtained from reduction of verbenone by $NaBH_4$.[7] *cis*-Verbenol is a solid compound with needle-like crystals, mp 68–70°C and *trans*-verbenol (**4**) is a liquid. Under air oxidation conditions (−)-α-pinene oxide (**3**) mostly

Table 1. The effect of the added base or acid (10%) on air oxidation of α-pinene catalysed by in situ generated [Co(II)Br_2–pyridine]-complex at 50°C after 22 h reaction time

	Composition of the product mixture (%)				
Base/acid	α-Pinene	α-Pinene oxide	*trans*-Verbenol	Verbenone	Other products
None	23	14	14	32	17
Pyridine	47	21	10	17	5
Glacial acetic acid	14	–	16	46	24

Table 2. The effect of glacial acetic acid on air oxidation of α-pinene catalysed by [Co(4-methylpyridine)$_2$$Br_2$] at 60°C

		Composition of the product mixture (%)				
Acid (vol%)	*h*	α-Pinene	α-Pinene oxide	*trans*-Verbenol	Verbenone	Other products
2	10	62	14	10	11	3
5	10	51	16	12	15	6
10	10	31	–	14	31	24
20	10	33	–	14	32	24

rearranged to α-campholene aldehyde (**5**). Other notable products were *trans*-pinocarveol (**6**), *trans*-carveol (**7**) and *trans*-sobrerol (**8**) (Scheme 1).

In the course of these experiments the (−)-α-pinene used came from separate lots. During air oxidations it was detected that fresh, unperoxidated α-pinene started to oxidise slower than a lot which contained peroxides. This indicates that peroxides, very often occurring in α-pinene, also participate in air oxidation as an initiator of the radical chain reaction.

Experimental

Catalysts were prepared as before and used without recrystallisation.[3]

A typical air oxidation experiment: (−)-α-Pinene (5.0 g, 0.037 mol) (99%, Fluka) air oxidation was performed in a thermostated glass reactor (bath 50–120°C) equipped with sintered gas inlet in the bottom and a reflux condenser. Co(II) catalyst (0.15 mol%) was added and molecular oxygen was passed through the reactor (5 ml/min) under atmospheric pressure.

Oxygen flow was controlled by Brooks Mass Flow Meter Model 5850TR. Progress of the reaction was monitored by TLC (on silica gel 60 F_{254} plates from Merck) and GC (Perkin–Elmer AutoSystem XL™, column OV-1701, length 25 m, i.d. 0.25 mm, phase layer 0.25 μm). The TLC chromatograms were visualised by UV light and staining with ethanolic anisaldehyde/glacial acetic acid/H_2SO_4 reagent. Reaction temperatures refer to bath temperatures.

Air oxidation products for identification were separated by flash chromatography (SiO_2 or neutral Al_2O_3, eluent hexane–ethyl acetate, 20:1) and they were identified by the ^1H and ^{13}C NMR [Bruker AM200 and DRX500 spectrometer operating at 200 and 500 MHz (for ^1H), respectively], GC–MS spectra (Kratos MS 80 mass spectrometer and Varian Saturn 2000) or by comparison with the authentic sample.

(1*S*)-(−)-Verbenone (4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one) (1). ^1H NMR (200 MHz, $CDCl_3$) δ 5.73 (q, 1H, *J*=1.5 Hz, H-3), 2.81 (dt, 1H, *J*=9.1, 5.5 Hz, H-7a), 2.65 (td, 1H, *J*=5.9, 1.5 Hz, H-5), 2.42 (td, 1H, *J*=6.5, 1.4 Hz, H-1), 2.08 (d, 1H, *J*=9.1 Hz, H-7b), 2.02 (d, 3H, *J*=1.5 Hz, H-10), 1.50 (s, 3H, H-8), 1.02 (s, 3H, H-9). Lit.[8] ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.8 (C-4), 170.0 (C-2), 121.2 (C-3), 57.6 (C-5), 53.9 (C-6), 49.7 (C-1), 40.8 (C-7), 26.6 (C-8), 23.5 (C-10), 22.0 (C-9). Lit.[8b] MS [*m*/*z* (relative intensity %)]: 150 (58, $M^{+\cdot}$), 135 (76), 122 (28), 121 (10), 119 (10), 115 (6), 109 (23), 108 (24), 107 (100), 105 (27), 95 (17), 93 (17), 91 (80), 80 (23), 79 (57), 77 (37), 67 (19), 65 (26), 55 (20), 53 (15), 51 (25), 50 (20), 41 (25), 39 (63). Lit.[9] $[\alpha]_D^{20}=-258°$ (*c* 1.0, CH_3Cl). HMRS: Found: 150.1044. Calcd for $C_{10}H_{11}O$, 150.1045.

Isolated α-pinene oxide (**3**) was identified by comparison of its GC retention time with the authentic sample.

(−)-*trans*-Verbenol (4,6,6,-trimethylbicyclo[3.1.1]hept-3-en-2-ol) (4). ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (m, 1H, *J*=3.1, 1.5 Hz, H-3), 4.24 (m, 1H, *J*=3.1, 1.5 Hz, H-4), 2.23 (m, 1H, *J*=9.1, 5.5 Hz, H-7a), 2.15 (tdd, 1H, *J*=5.7, 1.8 Hz, H-5), 2.00 (td, 1H, *J*=5.4, 1.3 Hz, H-1) 1.70 (t, 3H, *J*=1.6 Hz, H-10), 1.30 (s, 3H, H-8), 1.26 (m, 1H, H-7b), 0.85 (s, 3H, H-9). Lit.[10] ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7 (C-2), 118.8 (C-3), 70.4 (C-4), 48.1 (C-1), 47.1 (C-5), 46.2 (C-6), 28.6 (C-7), 26.6 (C-8), 22.5 (C-10), 20.4 (C-9). Lit.[8b] MS [*m*/*z* (relative intensity %)]: 152 (9, $M^{+\cdot}$), 137 (12), 134 (8), 123 (8), 121 (9), 119 (22), 110 (13), 109 (55), 107 (13), 96 (13), 95 (42), 94 (40), 93 (23), 91 (50), 83 (95), 81 (53), 79 (48), 77 (40), 69 (66), 67 (53), 65 (20), 59 (12), 55 (100), 53 (20), 51 (18), 50 (21), 43 (18), 41 (68), 39 (91). Lit.[9] HMRS: Found: 168.1509. Calcd for $C_{11}H_{20}O$, 168.1514.

α-Campholene aldehyde [(2,2,3-trimethyl-3-cyclopentenyl)-ethanal] (5). ^1H NMR (200 MHz, $CDCl_3$) δ 9.76 (s, 1H, CHO), 5.19 (s, 1H, H-4), 2.57–1.75 (m, 5H), 1.57 (s, 3H, CH_3), 0.96 (s, 3H, gem. CH_3), 0.75 (s, 3H, gem. CH_3). Lit.[11] ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.8 (CHO), 147.9 (C-3), 121.5 (C-4), 46.8 (C-2), 45.0 (CH_2CHO), 44.1 (C-1), 35.4 (C-5), 25.5 (gem. CH_3), 19.9 (gem. CH_3), 12.5 (CH_3). Lit.[12] MS [*m*/*z* (relative intensity %): 137 (2, $M^{+\cdot}$), 119 (4), 109 (22), 108 (100), 95 (32), 93 (67), 91 (20), 81 (17), 79 (10), 77 (13), 67 (25), 55 (16), 53 (12), 51 (6), 43 (15), 41 (32), 39 (22). Lit.[9,11] MS [*m*/*z* (CI, NH_3)] 153 ($M+1^+$).

trans-Pinocarveol (**6**) was identified by comparison of its GC retention time with the authentic sample.

***trans*-Carveol [2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol] (7).** ^1H NMR (200 MHz, $CDCl_3$) δ 5.55 (d, *J*=5 Hz, 1H, H-3), 4.70 (m, 2H, =CH_2), 3.97 (m, 1H, H-1), 2.40–1.80 (m, 4H), 1.75 (m, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.54 (dt, *J*=13 Hz, *J*=4 Hz, 1H, H-5). Lit.[13] ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.1 (=C<), 134.2 (C-2), 125.1 (C-3), 108.9 (=CH_2), 68.4 (C-1), 36.7 (C-5), 35.1 (C-5), 30.9 (C-4), 20.8 (2×CH_3). MS [*m*/*z* (relative intensity %)]: 152 (10, $M^{+\cdot}$), 137 (12), 124 (10), 119 (22), 109 (100), 95 (18), 93 (18), 91 (31), 84 (85), 83 (35), 81 (15), 79 (15), 77 (20), 69 (33), 67 (18), 65 (13), 57 (20), 55 (48), 53 (22), 51 (13), 43 (28), 41 (62), 39 (52). Lit.[9]

***trans*-Sobrerol [4-(1-hydroxy-1-methylethyl)-2-methyl-2-cyclohexen-1-ol] (8).** ^1H NMR (200 MHz, $CDCl_3$) δ 5.51 (m_a, 1H, H-2), 4.05 (m_a, 1H, H-6), 3.62 (m_a, 1H, H-8), 1.77 (s, 3H, H-7), 1.20 (s, 3H, H-9 or -10), 1.17 (s, 3H, H-10 or -9). Lit.[11] MS [*m*/*z* (relative intensity %)]: 152 (12), 137 (18), 119 (6), 109 (60), 95 (18), 94 (23), 93 (18), 92 (20), 84 (10), 81 (12), 79 (57), 77 (11), 71 (10), 69 (12), 67 (10), 59 (100), 55 (18), 43 (79), 41 (33), 39 (20). Lit.[9,11]

***trans*-3-Pinen-2-ol (2,6,6,trimethylbicyclo[3.1.1]hept-3-en-2-ol) (9).** ^1H NMR (200 MHz, $CDCl_3$) δ 6.25 (dd, *J*=8.6 Hz, 1H, H-4), 5.49 (dd, *J*=8.6 Hz, *J*=2.2 Hz, 1 H, H-3), 2.44–1.98 (m, 3H), 1.45 (d, *J*=9.3 Hz, 1H, H-7b), 1.34 (s, 3H, H-8), 1.30 (s, 3H, H-10), 0.94 (s, 3H, H-9). Lit.[14] ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.0 (C-4), 129.9 (C-3), 74.1 (C-2), 54.0 (C-1), 46.9 (C-6), 42.7 (C-5), 33.3 (C-7), 26.9 (C-10), 25.7 (C-8), 24.1 (C-9). MS [*m*/*z* (relative

intensity %)]: 152 (4, $M^{+\cdot}$), 137 (18), 134 (7), 123 (4), 119 (22), 109 (100), 97 (26), 95 (53), 93 (43), 91 (71), 84 (21), 82 (40), 81 (37), 79 (46), 77 (44), 69 (56), 67 (91), 65 (30), 55 (27), 53 (24), 51 (22), 50 (21), 43 (89), 41 (52), 39 (77).

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References

1. Typical papers: (a) Mukaiyama, T.; Yamada, T. *Bull. Chem. Soc. Jpn* **1995**, *68*, 17, and references cited therein. (b) Iqbal, J.; Mukhopadhyay, M.; Mandal, A. K. *Synlett* **1997**, 876, and references cited therein. (c) Hamamoto, M.; Nakayama, K.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1993**, *58*, 6421. (d) Mizuno, N.; Hirose, T.; Tateishi, M.; Iwamoto, M. *Chem. Lett.* **1993**, 1839. (e) Mastrorilli, P.; Nobile, C. F.; Suranna, G. P.; Lopez, L. *Tetrahedron* **1995**, *51* 7943. (f) Nam, W.; Kim, H. J.; Kim, S. H.; Ho, R. Y. N.; Valentine, J. S. *Inorg. Chem.* **1996**, *35*, 1045. (g) Chavez, F. A.; Nguyen, C. V.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 6282. (h) Chavez, F. A.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1997**, *36*, 6323. (i) Chavez, F. A.; Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 9015. (j) Sugamoto, K.; Matsushita, Y.; Matsui; T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3989.

2. (a) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580. (b) Sethi, S.; Natu, A. D. *Ind. J. Chem.* **1986**, *25B*, 248. (c) Li, P.; Alper, H. *J. Mol. Catal.* **1992**, *72*, 143. (d) Rothenberg, G.; Yatziv, Y.; Sasson, Y. *Tetrahedron* **1998**, *45*, 593. (e) Romano, A. M.; Ricci, M. *J. Mol. Catal.* **1997**, *120*, 71.

3. Lajunen, M.; Koskinen, A. M. P. *Tetrahedron Lett.* **1994**, *35*, 4461.

4. Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*, Academic: New York, 1981 (and references therein).

5. (a) King, L. C.; Farber; H. *J. Org. Chem.* **1961**, *26*, 326. (b) Hartshorn; M. P.; Kirk, D. N.; Wallis, A. F. A. *J. Chem. Soc.* **1964**, 5494. (c) Isaeva, Z. G.; Bakaleinik, G. A. *Dokl. Akad. Nauk SSSR* **1967**, *176*, 1310. (d) Joshi, V. S.; Damodaran, N. P.; Dev, S. *Tetrahedron* **1971**, *27*, 475.

6. (a) Hata, E.; Takai, T.; Mukaiyama, T. *Chem. Lett.* **1993**, 1513. (b) Reetz, M.; Töllner, K. *Tetrahedron Lett.* **1995**, *36*, 9461.

7. Gemal, A.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

8. Watanabe, M.; Bahlul, Z. A.; Michiharu, K. *J. Org. Chem.* **1993**, *58*, 3923. (b) Farooq, A.; Hanson, J. R. *Phytochemistry* **1995**, *40*, 815.

9. Adams, R. P. *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*, Allured Publishing Corporation: Carol Stream, IL, 1995.

10. Cooper, M. A.; Salmon, J. R.; Whittaker, D.; Scheidegger, U. *J. Chem. Soc. (B)* **1967**, 1259.

11. Vinckier, C.; Compernolle, F.; Saleh, A. M. *Bull. Soc. Chim. Belg.* **1997**, *106*, 501.

12. Bohlmann, F.; Zeisberg, R. *Org. Magn. Reson.* **1975**, *7*, 426.

13. Yasui, K.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1995**, *60*, 1365.

14. Jefford, C. W.; Boschung, A. F.; Moriarty, R. M.; Rimbault, C. G.; Laffer, M. H. *Helv. Chim. Acta* **1973**, *56*, 2649.