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Catalytic aerobic oxidation of alcohols by $Fe(NO_3)_3$–$FeBr_3$

Sandra E. Martín* and Darío F. Suárez

INFIQC, Dpto. de Química Orgánica, Fac. de Ciencias Químicas, Universidad Nacional de Córdoba, Cdad Universitaria,
5000 Córdoba, Argentina

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Abstract—Selective aerobic oxidation of secondary and benzylic alcohols was efficiently accomplished by the binary catalyst system $Fe(NO_3)_3$–$FeBr_3$ under *air* at room temperature. The oxidation developed in mild conditions and showed good yields. A secondary alcohol even in the presence of a primary one was selectively oxidized. © 2002 Elsevier Science Ltd. All rights reserved.

The oxidation of alcohols plays an important role in organic synthesis. New ways to achieve this transformation continue to receive attention in spite of the availability of numerous other oxidizing reagents.[1] Unfortunately, one or more equivalents of these often hazardous or toxic oxidizing reagents is required. In terms of economical benefit and environmental impact, catalytic oxidations processes are extremely valuable and those involving molecular oxygen or air are particularly attractive.[2] Although a variety of different catalytic systems for the aerobic oxidation of alcohols has been developed[3] many applications are often restricted to activated substrates.[4] A number of ruthenium-based catalytic systems using air or molecular oxygen have been reported.[4f,5] Otherwise, catalytic oxidations of alcohols in the presence of molecular oxygen as sole oxidant or with additional co-oxidants takes place using Cu,[4a,6] Pd,[4c,e,7] Co,[8] Pt,[9] Os[10] and recently Ni[11] catalysts. There are few examples of heterogeneous catalysts with molecular oxygen for the oxidation of alcohols.[4c,5c,7f–g,12] Recently, new methods including molecular oxygen oxidation catalyzed by bifunctional system such as $(n\text{-}Pr_4N)(RuO_4)$–CuCl,[13] OsO_4–CuCl[14] or related heterobimetallic complexes have been reported.[15] Additionally, Mn–Co and Mn–Cu nitrates in combination with TEMPO allow the oxidation of alcohols by oxygen.[16] Although the direct use of atmospheric pressure of air is more desirable not many examples have been reported.[17] The search for catalytic systems that use inexpensive, nontoxic, molecular oxygen in the air as secondary oxidant remains an important challenge. On the other hand, clay-supported metallic nitrates have been widely used as reagents in organic synthesis, particularly in the field of oxidation and nitration.[18] The reactivity of Fe(III) montmorillonite-supported metal nitrates (Clayfen) towards organic substrates has been extensively studied.[19] Clayfen is unstable, but may be stored for a few days under pentane and the preparation of the compound also needs certain caution.[18a,b] Several methods for the oxidation of alcohols with metal nitrates have been described.[20] Such systems include clay-supported Fe(III) nitrate,[20a,b] in situ generated montmorillonite K-10 supported Fe(III) nitrate[20d] and metallic nitrates supported on silica gel.[20c,e] Varma and Dahiya described the microwave-assisted oxidation of alcohols with Clayfen under solvent-free conditions.[21] In all these cases the metal nitrates were used as reagent; and in some of these cases it was claimed that they acted as a source of nitrosonium ions.[18a,20a] The oxidation of benzyl alcohol by montmorillonite-supported metal nitrates in an NO_3^-–alcohol ratio of 0.5 was also investigated.[22]

The aim of our work was to develop a simple and general procedure for the oxidation of non-activated alcohols catalyzed by iron. In a previous work, we reported a very efficient and selective aerobic oxidation of sulfides to sulfoxides with the binary system $Fe(NO_3)_3$–$FeBr_3$,[23] developed under mild conditions, yielding high purity products, that may be applied to any type of dialkyl and alkyl aryl sulfide, and to substrates of biological interest. Taking all this into account, we report here our recent findings on the oxidation of alcohols with the same binary catalyst $Fe(NO_3)_3$–$FeBr_3$, with air under mild conditions. The advantage of this method is that it does not demand a metal complex or any co-oxidant. Aerobic catalytic oxidation of alcohols was carried out in CH_3CN, at room temperature in the presence of $Fe(NO_3)_3{\cdot}9H_2O$–

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* Corresponding author. E-mail: martins@dqo.fcq.unc.edu.ar

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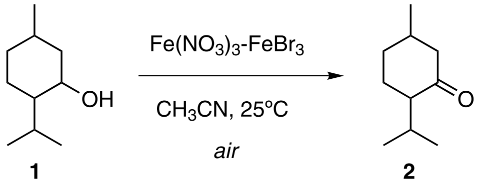
$FeBr_3$ as catalysts. Menthol (1) was selected as a model substrate for the optimization process (Eq. (1)).



(1)

A typical experimental procedure was quite simple: To 0.1 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.05 mmol $FeBr_3$ in CH_3CN (5 mL) was added 1 mmol of the substrate. The reaction mixture was stirred under air at room temperature. Yields were determined either by gas chromatography using an internal standard or products were isolated by column chromatography with appropriate combination of hexane/ethyl acetate. Table 1 shows results of the oxidation of menthol (**1**) under different conditions and catalytic systems. The oxidation of **1** afforded menthone (**2**) at 85% yield with total selectivity within 24 h (entry 1, Table 1). No other products were obtained. Compound **2** was isolated yielding 81 and 14% of **1** was recovered. Among the solvents examined, CH_3CN was found to be the most effective. Reaction in solvents such as benzene, CH_2Cl_2 and AcOEt produced unfavorable results.

In order to improve the efficiency of this catalytic system we examined different ratios between the metallic salt and the metal bromide. The best results were found when the ratio between the salts $Fe(NO_3)_3$:$FeBr_3$ was 1:0.5, similar to the oxidation reaction of sulfides.[23]

Table 1. Catalytic air oxidation of menthol (**1**) to menthone (**2**) at room temperature[a]

Entry	Catalyst (% mmol)	Conditions	Yield of **2**[b] (%)
1	$Fe(NO_3)_3$[c]–$FeBr_3$	Air	85
2	$Fe(NO_3)_3$	Air	26
3	$FeBr_3$	Air	2
4	$Fe(NO_3)_3$–$FeBr_3$	O_2[d]	82
5	$Fe(NO_3)_3$–$FeBr_3$	N_2[d]	22
6	$Fe(NO_3)_3$–$[(FeBr_3)_2(DMSO)_3]$[e]	Air	60
7	$Fe(NO_3)_3$–KBr	Air	2
8	$Fe(NO_3)_3$–$FeCl_3$	Air	24
9	$Cu(NO_3)_2$[f]–$CuBr_2$	Air	10
10	$Zn(NO_3)_2$[g]–$ZnBr_2$	Air	N.R.[h]

[a] Reaction carried out with 1 mmol of substrate in an open system at room temperature for 24 hours, at a molar ratio substrate:$Fe(NO_3)_3$:$FeBr_3$ 1:0.1:0.05 mmol, in 5 mL of CH_3CN. The reaction has been shown to be effective on a 35 mmol scale with no change in reactivity or yields.

[b] Determined by GC.

[c] $Fe(NO_3)_3$ corresponds to $Fe(NO_3)_3{\cdot}9H_2O$.

[d] Under an O_2 or N_2 atmosphere (1 atm).

[e] Reaction carried out for 36 h.

[f] $Cu(NO_3)_2$ corresponds to $Cu(NO_3)_2{\cdot}2.5H_2O$.

[g] $Zn(NO_3)_2$ corresponds to $Zn(NO_3)_2{\cdot}6H_2O$.

[h] N.R.: Reaction did not occur.

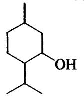
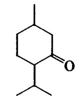
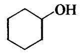
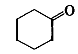
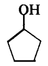
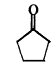
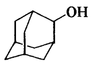
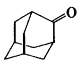
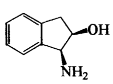
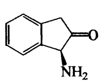
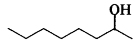
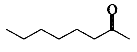
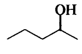
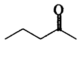
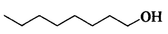
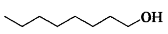
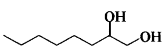
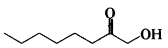
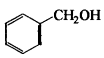
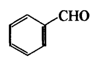
When $Fe(NO_3)_3$ was used as catalyst alone, only 26% of the alcohol was oxidized to ketone and the rest was recovered intact (entry 2, Table 1). This is in agreement with previous reports of metal nitrates used as oxidation reagents.[20] When $FeBr_3$ was added to the system, the rate of oxidation was enhanced and the system became catalytic. Oxidation with only $FeBr_3$ under the same conditions resulted in practically no reaction, and **1** remained unchanged (entry 3, Table 1). The use of less than 10 mol% $Fe(NO_3)_3$ took longer to react. Next, the effect of the temperature was examined. No improved rates could be observed at higher temperatures. The formation of **2** under a dioxygen atmosphere proceeded in the same way as in air (entry 4, Table 1). Otherwise, under a nitrogen atmosphere, only 22% of **1** was oxidized and the rest was recovered (entry 5, Table 1). Oxidation with only $Fe(NO_3)_3$ under nitrogen atmosphere took place in the same way as in air. As previously reported in the oxidation reactions with $Fe(NO_3)_3$, the metal nitrates are a source of nitronium ions,[18,20a] thus the reaction did not require molecular oxygen. Therefore, oxidation observed in the reactions above described under nitrogen atmosphere could be due to this pathway. However, during the catalytic reaction the latter results hint at the possibility that dioxygen was involved in the course of the reaction. It is interesting to note that the reaction does not require a high pressure of dioxygen. In fact, it can be run at atmospheric pressure of air. This is an important feature of this reaction. On the other hand, the aerobic oxidation of **1** by $Fe(NO_3)_3$ and the complex $[(FeBr_3)_2(DMSO)_3]$[24] was examined, (entry 6, Table 1). The main advantage of the use of this coordination compound is its high stability unlike that of anhydrous $FeBr_3$. This complex was found to be less efficient than $FeBr_3$, even at longer reaction times. We also investigated the role of components of the binary catalyst in this oxidizing system. The catalytic reaction proceeded hardly varying from $FeBr_3$ to KBr (entry 7, Table 1). This result shows that the oxidation of the substrate is related to the Fe(III) of the metal halide, and that in a special manner this Fe(III) controls oxidation. This is further supported by the results of the reaction carried out with $Fe(NO_3)_3$–$[(FeBr_3)_2(DMSO)_3]$. As previously discussed,[23] the presence of a ligand delayed oxidation, which means that the metal center was less available for the coordination of the substrate. Furthermore, it was found that replacing $FeBr_3$ by $FeCl_3$ led to very little catalytic activity, even though it contained Fe(III) (entry 8, Table 1). This is in agreement with the result shown in the oxidation of sulfides with nitric acid in a biphasic system catalyzed by $FeBr_3$ and $FeCl_3$[25] or by tetrabromoaurate(III) and tetrachloroaurate,[26] in which lower yields were obtained in the oxidation involving chlorides. Although, there was practically no reaction with KBr, the last finding with $FeCl_3$ confirmed the catalytic role of the bromide together with Fe(III). In the absence of either Fe(III) or bromide the oxidation hardly occurred. The catalytic activity of $Cu(NO_3)_2$–$CuBr_2$ and $Zn(NO_3)$–$ZnBr_2$ systems was also examined (entries 9–10, Table 1). In the Cu(II) system **2** was obtained in low amounts while the oxidation of **1** did not occur with $Zn(NO_3)_2$–$ZnBr_2$ as catalyst.

Having established what appeared to be the optimal conditions, we switched our attention to the substrate. A variety of alcohols were then reacted with this remarkably simple procedure and the results appear in Table 2. As shown, both secondary and benzylic alcohols were oxidized in good yields. All the reactions occurred with complete selectivity for ketones or aldehyde and no over-oxidation or other products were detected in the reaction mixtures. The products could be readily isolated. The only purification step consisted of a filtration through a silica gel column, which led to good yields and purity of the products. It is important to notice that the reaction works well with sterically hindered alcohols such as menthol (entry 1, Table 2). Many other secondary cyclic alcohols were efficiently oxidized (entries 2–5, Table 2). The 2-adamantanol required longer reaction times for the same conversion than other cyclic alcohols (entry 4, Table 2).

Interesting results were obtained during the oxidation of (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (entry 5, Table 2). The presence of an amino group in the substrate did not interfere with the oxidation process. The oxidation product was obtained in good yields with no change in the configuration at the carbon atom bond bearing the amino group. Aerobic oxidation can also be successfully performed with other aliphatic secondary alcohols (entries 6–7, Table 2). It should be noticed as a very interesting finding that primary alcohols could not be oxidized by this system (entry 8, Table 2). Besides, secondary alcohols were selectively oxidized even in the presence of primary ones (entry 9, Table 2). The reason for this behavior is not clear so far. However, using ruthenium-hydrotalcites as catalysts Kaneda has reported that primary aliphatic alcohols are barely oxidized while secondary ones smoothly convert into their corresponding ketona.[12b] The oxidation of benzyl alcohol produced benzaldehyde in good yield with no over-oxidation (entry 10, Table 2).

The present aerobic oxidation can be rationalized by two different active species in the catalytic cycle. Since the reaction mixture became light brown NO_2 may be generated in situ, as proposed in a related system which contained NO_3^- and MBr_3.[27] Thus, the $Fe(NO_3)_3$–$FeBr_3$ system could be a source of NO_2 and might play a role in this oxidation. On the other hand, mechanistic studies by electrochemical methods demonstrated that in selective oxidation of sulfides with nitric acid catalyzed by $FeBr_3$ and $[(FeBr_3)_2(DMSO)_3]$ the high selectivity exhibited was controlled by the transition metal, the role of nitric acid was to oxidize bromides into bromine, and that this couple was the redox mediator in sulfide oxidation.[25] In our system the catalytic role of bromides and the control of oxidation by Fe(III) was also confirmed. Furthermore, the oxidation potential of the nitrates is too low for an efficient oxidation of chloride into chlorine.[25] This fact may account for the low yields obtained from the oxidations by $Fe(NO_3)_3$–

Table 2. Selective aerobic oxidation of alcohols using $Fe(NO_3)_3$–$FeBr_3$ as catalyst[a]

Entry	Substrate	Product[b]	Isolated yield[c] (%)
1			81
2			80
3			77
4[d]			80
5			85
6			75
7			78
8			N.R.[e]
9			74
10			80

[a] Reaction carried out with 1 mmol of the substrate in 5 mL of CH_3CN in an open system at room temperature, for 24 hours, in a molar ratio substrate:$Fe(NO_3)_3$:$FeBr_3$ 1:0.1:0.05 mmol. [b] Spectral data were in agreement with the proposed structure and with literature data. [c] Yields were calculated on the starting alcohol and evidenced on the pure isolated products. [d] Reaction carried out for 36 hours. [e] N.R: Reaction did not occur.

$FeCl_3$ system. Thus, an oxidation should be considered where the active oxidant could be the bromide/bromine couple and the alcohols were activated by coordination to the metal.

In conclusion, the catalytic system $Fe(NO_3)_3$–$FeBr_3$ led to an effective and selective oxidation of secondary and benzylic alcohols using atmospheric pressure of air as a sole oxidant. Secondary alcohols are selectively oxidized even in the presence of primary ones. The reaction proceeded under very mild conditions and it was easy to implement. Two types of active species may be regarded in the metal-catalyzed oxidation, either oxidation by NO_2, or oxidation by the bromide/bromine couple controlled by Fe(III).

General procedure. Oxidation reactions catalyzed by $Fe(NO_3)_3$–$FeBr_3$. A typical experiment was carried out in an open reaction tube provided with a condenser. To the mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (0.1 mmol) and $FeBr_3$ (0.05 mmol) in 5 mL of CH_3CN menthol was added (1 mmol). The reaction mixture was stirred under aerial conditions at room temperature. GC was used to follow the reaction. When the reaction was complete, CH_2Cl_2 was added and the two phases were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was chromatographed on a silica gel (70–270 mesh ASTM) column, and eluted with ethyl acetate/hexanes using various ratios. All products identified were found to be identical to authentic samples.

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References

1. (a) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 6; (b) Hudlick, M. *Oxidation in Organic Chemistry*; ACS Monographs 186, Washington, DC 1990; (c) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M.; Ley, S. V., Eds.; Pergamon: Oxford, 1991; Vol. 7, p. 251.
2. Simándi, L. I. In *Catalytic Activation of Dioxygen by Metal Complexes*; Ugo, R; James, B. R., Eds.; Kluwer Academic: Dordrecht, 1992.
3. Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157.
4. (a) Semmelhack, M. F.; Schmid, C. R.; Cortés, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374; (b) Bäckvall, J.-E.; Chowdhury, R. L.; Karlsson, U. *J. Chem. Soc., Chem. Commun.* **1991**, 473; (c) Kaneda, K.; Fujie, Y.; Ebitani, K. *Tetrahedron Lett.* **1997**, *38*, 9023; (d) Kaneda, K.; Yamashita, T.; Matsushita, T.; Ebitani, K. *J. Org. Chem.* **1998**, *63*, 1750; (e) Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 3185; (f) Lee, M.; Chang, S. B. *Tetrahedron Lett.* **2000**, *41*, 7507.
5. (a) Wang, G.-Z.; Andeasson, U.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1994**, *1*, 1037; (b) Inokuchi, T.; Nakagawa, K.; Torii, S. *Tetrahedron Lett.* **1995**, *36*, 3223; (c) Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Chellé-Regnaut, I.; Urch, C. J.; Brown, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 12661; (d) Lenz, R.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3291; (e) Hinzen, B.; Lenz, R.; Ley, S. V. *Synthesis* **1998**, 977; (f) Hanyu, A.; Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1998**, *39*, 5557; (g) Matsutani, K.; Uchida, T.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2000**, *41*, 5119; (h) Dijksman, A.; MarinoGonzales, A.; Payeras, A. M. I.; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 6826; (i) Csjernyik, G.; Ell, A. H.; Fadini, L.; Pugin, B.; Backvall, J. E. *J. Org. Chem.* **2002**, *67*, 1657.
6. (a) Liu, X.; Qui, A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1993**, *115*, 3239; (b) Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. *Science* **1996**, *274*, 2044; (c) Betzemeier, B.; Cavazzini, M.; Quici, S.; Knochel, P. *Tetrahedron Lett.* **2000**, *41*, 4343; (d) Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Chellé-Regnaut, I.; Gautier, A.; Brown, S. M.; Urch, C. J. *J. Org. Chem.* **1999**, *64*, 2433; (e) Markó, I. E.; Gautier, A.; Mutonkole, J.-L.; Dumeunier, R.; Ates, A.; Urch, C. J.; Brown, S. M. *J. Organomet. Chem.* **2001**, *624*, 344.
7. (a) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157; (b) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **1998**, *39*, 6011; (c) Nagata, H.; Ogasawara, K. *Tetrahedron Lett.* **1999**, *40*, 6617; (d) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636; (e) Besson, M.; Callezot, P. *Catal. Today* **2000**, *57*, 127; (f) Nishimura, T.; Kakiuchi, N.; Inoue, M.; Uemura, S. *Chem. Commun.* **2000**, 1245; (g) Kakiuchi, N.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Org. Chem.* **2001**, *66*, 6620.
8. (a) Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1989**, 519; (b) Iwahama, T.; Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *Tetrahedron Lett.* **1995**, *36*, 6923; (c) Iwahama, T.; Yosino, Y.; Keitoku, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2000**, *65*, 6502; (d) Fernandez, I.; Pedro, J. R.; Rosello, A. L.; Ruiz, R.; Castro, I.; Ottenwaelder, X.; Jounaux, Y. *Eur. J. Org. Chem.* **2001**, *7*, 1235.
9. Jia, C.-G.; Jing, F.-Y.; Hu, W.-D.; Huang, M.-Y.; Jiang, Y.-Y. *J. Mol. Catal.* **1994**, *91*, 139.
10. (a) Zhang, N.; Mann, C. N.; Shapley, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 6591; (b) Dobler, C.; Mehltretter, G. M.; Sundermeier, U.; Eckert, M.; Militzer, H. C.; Beller, M. *Tetrahedron Lett.* **2001**, *42*, 8447.
11. Choudary, B. M.; Kantam, M. L.; Rahman, A.; Reddy, C. V.; Rao, K. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 763.
12. (a) Vocanson, F.; Guo, Y. P.; Namy, J. L.; Kagan, H. B. *Synth. Commun.* **1998**, *28*, 2577; (b) Matsushita, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **1999**, 265; (c) Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, *122*, 7144; (d) Pagliaro, M.; Ciriminna, R. *Tetrahedron Lett.* **2001**, *42*, 4511.
13. Coleman, K. S.; Lorber, C. Y.; Osborn, J. A. *Eur. J. Inorg. Chem.* **1998**, 1673.

14. (a) Coleman, K. S.; Coppe, M.; Thomas, C.; Osborn, J. *Tetrahedron Lett*. **1999**, *40*, 3723; (b) Muldoon, J.; Brown, S. N. *Org. Lett*. **2002**, *4*, 1043.
15. (a) Murahashi, S.-I.; Naota, T.; Hirai, N. *J. Org. Chem*. **1993**, *58*, 7318; (b) Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H.-C. *J. Am. Chem. Soc*. **2000**, *122*, 1079; (c) Lorber, C. Y.; Smidt, S. P.; Osborn, J. A. *Eur. J. Inorg. Chem*. **2000**, *4*, 655.
16. Cecchetto, A.; Fontana, F.; Minisci, F.; Recupero, F. *Tetrahedron Lett*. **2001**, *42*, 6651.
17. Aerobic oxidation using air, for examples see: 5a,c,g; 6b,d,e; 7c–e,g; 14b; 15a.
18. (a) Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909; (b) Cornelis, A.; Laszlo, P. *Aldrichimica* **1988**, *21*, 97; (c) Nishiguchi, T.; Bougauchi, M. *J. Org. Chem*. **1990**, *55*, 5606; (d) Tsubokawa, N.; Kimoto, T.; Endo, T. J. *Mol. Cat. A; Chem*. **1995**, *101*, 40; (e) Békássy, S.; Cseri, T.; Horváth, M.; Farkas, J.; Figueras, F. *New. J. Chem*. **1998**, 339.
19. (a) Heravi, M. M.; Ajami, D.; Mojtahedi, M. M.; Ghassemzadeh, M. *Tetrahedron Lett*. **1999**, *40*, 561; (b) Firouzabadi, H.; Iranpoor, N.; Zolfigol, M. A. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2169; (c) Békássy, S.; Cseri, T.; Bódás, Z.; Figueras, F. *New. J. Chem*. **1996**, *20*, 357.
20. (a) Cornelis, A.; Laszlo, P. *Synthesis* **1980**, 849; (b) Cornelis, A.; Herzé, P.-Y.; Laszlo, P. *Tetrahedron Lett*. **1982**, *23*, 5035; (c) Nishiguchi, T.; Asano, F. *J. Org. Chem*. **1989**, *54*, 1531; (d) Hirano, M.; Komiya, K.; Morimoto, T. *Oppi Briefs* **1995**, *27*, 703; (e) Khadilkar, B.; Borkar, S. *Synth. Commun*. **1998**, *28*, 207.
21. Varma, R. S.; Dahiya, R. *Tetrahedron Lett*. **1997**, *38*, 2043.
22. Cseri, T.; Békássy, S.; Figueras, F. *Bull. Soc. Chim. Fr*. **1996**, *133*, 547.
23. Martín, S. E.; Rossi, L. I. *Tetrahedron Lett*. **2001**, *42*, 7147.
24. (a) Suárez, A. R.; Rossi, L. I. *Sulfur Lett*. **1999**, *23*, 89; (b) Suárez, A. R.; Rossi, L. I. *Sulfur Lett*. **2000**, *24*, 73; (c) Riley, D. P.; Lyon, J., III *J. Chem. Soc., Dalton Trans*. **1991**, 157.
25. Suárez, A. R.; Baruzzi, A. M.; Rossi, L. I. *J. Org. Chem*. **1998**, *63*, 5689.
26. Gasparrini, F.; Giovannoli, M.; Misiti, D.; Giovanni, N.; Palmieri, G. *J. Org. Chem*. **1990**, *55*, 1323.
27. Komatsu, M.; Uda, M.; Suzuki, H. *Chem. Lett*. **1997**, 1229.