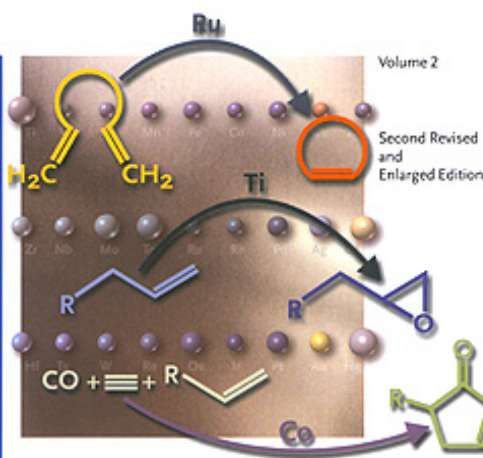


Edited by
Matthias Beller and Carsten Bolm

WILEY-VCH

Transition Metals for Organic Synthesis

Building Blocks and Fine Chemicals



The definitive standard reference on the topic—now in its second, enlarged edition.

The two-volume "Beller/Bolm" presents the numerous applications in both academic and industrial research in a clearly structured manner. The fundamentals, catalytic and stoichiometric reactions with transition metals such as hydroformylation, amidocarbonylation and the Pauson-Khand reaction are treated in the first volume. The second volume focuses on hydrogenations and oxidations, as well as more modern methods, including the use of microwaves or ionic liquids.

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Matthias Beller, born in 1972, studied chemistry at the Georg-August-University of Göttingen, Germany, where he completed his doctoral thesis on the "Development and Application of New Methods for Synthesis of Anti-Tumor Drugs and Antiviral Agents" in 1995 in the group of Prof. C. F. Mayo. As recipient of a Lehigh Scholarship from the Association of the German Chemical Industry, he then spent a one-year postdoctoral fellowship in the working group of Prof. K. I. Ivin at the Massachusetts Institute of Technology in Cambridge, Massachusetts. From 1997 to 1999, Beller was an employee of BASF AG, where he directed the "Hydrogenation Catalysis" project in the company's central research unit. At the beginning of 1999 he moved to the Technical University of Munich (TUM), Professor for Organic Chemistry. Two and a half years later he returned to the University of Bonn to head the Leibniz Institute for Organic Catalysis (IOC) and to occupy a Chair in catalysis.

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Carsten Bolm was born in Braunschweig in 1970. He studied chemistry at the TU Braunschweig (Germany) and at the University of Wisconsin, Madison (USA). In 1991 he obtained his doctorate with Professor Kocienski in Marburg (Germany). After postdoctoral training with Professor Martinelli at MIT, Cambridge (USA), Carsten Bolm worked in Basel (Switzerland) with Professor Crotti to obtain his habilitation. In 1995 he became Professor of Organic Chemistry at the University of Marburg (Germany), and since 1999 he has a chair of Organic Chemistry at the RWTH Aachen (Germany). His awards include the Young Master Catalyst prize, the ACS Catalysis Award for Habilitation, the annual prize for Chemistry of the Academia der Wissenschaften zu Göttingen, the Otto-Röping prize, and the Otto-Röping award, the first award of the University of Marburg (USA), Bonn (Germany), Vienna (Austria), Milano (Italy), and Namur (Belgium), and the award of the Japan Society for the Promotion of Science (JSPS).

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Volume 2 of 2

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Second Revised and Enlarged Edition
Volume 2

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The following is a fragment (Chapter 2.2, Vol. 2) from the book:

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Preface to the Second Edition

Is there really a need for a second edition of a two-volume book on the use of Transition Metals in Organic Synthesis after only 6 years? How will the community react? Are there going to be enough interested colleagues, who will appreciate the effort (and spend their valuable money in times of shortened budgets)? Do we, the editors, really want to invest into a project, which, for sure, will be most time-consuming? All of these questions were asked about three years ago, and together with Wiley/VCH we finally answered them positively. Yes, there has been enough progress in the field. Yes, the community will react positively, and yes, it is worth spending time and effort in this project, which once more will show and underline the strength of modern transition metal chemistry in organic synthesis.

The Nobel Prize in Chemistry 2001, which was awarded to K. Barry Sharpless, Ryoji Noyori (who both are authors in this book), and William S. Knowles for their contributions in asymmetric catalysis, nicely highlighted the area and demonstrated once more the high synthetic value of the use of transition metals for both small-scale laboratory experiments and large-scale industrial production.

During the past six years the field has matured and at the same time expanded into areas, which were rather unexplored before. Taking this development into account we decided to pursue the following concept: On the one hand the authors of the first edition were asked to up-date their original chapters, and most of them kindly responded positively. In a few cases the contributions of the first edition were reused and most often up-dated by an additional chapter written by another author. Some fields are now covered by other authors, which proved most interesting, since the same topic is now presented from a different perspective. New research areas have been summarized by younger active colleagues and leading experts.

It should be clearly stated that the use of transition metals in organic synthesis can not be fully covered even in a two-volume set. Instead, the present book presents a personal selection of the topics which we believe are the most interesting and actual ones. In general, the focus of the different contributions is on recent research developments since 1998. Literature up to mid – sometimes end – of 2003 has been taken into account. Hence, we believe the new book complements nicely the first more general edition of this book.

Most importantly, as editors we thank all contributors for their participation in this project and, in some case, for their patience, when it took longer than expected. We also acknowledge the continuous stimulus by Elke Maase from Wiley/VCH, who did not push but challenged. It remains our hope that the readers will enjoy reading the new edition and discover aspects, which will stimulate their own chemistry and create ideas for further discoveries in this most timely and exciting area of research and science.

Aachen, June 2004
Rostock, June 2004

Carsten Bolm
Matthias Beller

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1.4.2.1.2	Iridium Catalysts	186
1.4.2.1.3	Ruthenium Catalysts	186
1.4.2.1.4	Copper Catalysts	186
1.4.2.1.5	Titanium Catalysts	187
1.4.2.2	Hydrosilylation of Imine Compounds	188
1.4.2.2.1	Rhodium Catalysts	188
1.4.2.2.2	Titanium Catalysts	188
1.4.2.2.3	Ruthenium Catalysts	189
1.5	Transition Metal-Catalyzed Hydroboration of Olefins	193
	<i>Gregory C. Fu</i>	
1.5.1	Introduction	193
1.5.2	Catalytic Asymmetric Hydroboration of Olefins	193
1.5.3	Applications of Transition Metal-Catalyzed Hydroboration in Synthesis	196
1.5.4	Transition Metal-Catalyzed Hydroboration in Supercritical CO ₂	197
1.5.5	Summary	198
2	Oxidations	199
2.1	Basics of Oxidations	201
	<i>Roger A. Sheldon and Isabel W.C.E. Arends</i>	
2.1.1	Introduction	201
2.1.2	Free-Radical Autoxidations	202
2.1.3	Direct Oxidation of the Substrate by the (Metal) Oxidant	205
2.1.4	Catalytic Oxygen Transfer	207
2.1.5	Ligand Design in Oxidation Catalysis	210
2.1.6	Enantioselective Oxidations	211
2.1.7	Concluding Remarks	211
2.2	Oxidations of C–H Compounds Catalyzed by Metal Complexes	215
	<i>Georgiy B. Shul'pin</i>	
2.2.1	Introduction	215
2.2.2	Oxidation with Molecular Oxygen	219
2.2.3	Combination of Molecular Oxygen with a Reducing Agent	224
2.2.4	Hydrogen Peroxide as a Green Oxidant	226
2.2.5	Organic Peroxy Acids	230
2.2.6	Alkyl Hydroperoxides as Oxidants	231
2.2.7	Oxidation with Sulfur-containing Peroxides	231
2.2.8	Iodosobenzene as an Oxidant	233
2.2.9	Oxidations with Other Reagents	235
2.3	Allylic Oxidations	243
2.3.1	Palladium-Catalyzed Allylic Oxidation of Olefins	243
	<i>Helena Grennberg and Jan-E. Bäckvall</i>	

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2.2

Oxidations of C–H Compounds Catalyzed by Metal Complexes

Georgiy B. Shul'pin

2.2.1

Introduction

Selective and efficient oxidative functionalization of aliphatic C–H bonds is one of the very important goals of organic chemistry. However, a practical realization of this task meets serious difficulties, especially in the case of saturated hydrocarbons, because of to the extremely high inertness of alkanes (which are the “noble gases of organic chemistry”). Alkanes do not usually react with “normal” reagents that easily oxidize much more reactive olefins, alcohols, amines etc. The usual solvents for organic synthesis, such as alcohols or ketones, are often not appropriate for reactions with saturated hydrocarbons, since a solvent and not a substrate is oxidized in this case. Moreover, alkanes are oxygenated to give products which are more reactive than the starting substrates, and naturally, if an excess of an oxidant is used, substantial over-oxidation to give undesirable compounds will take place.

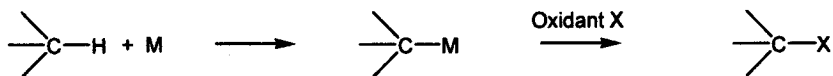
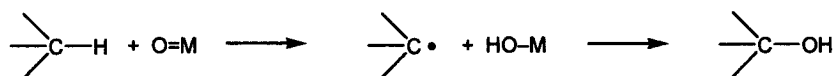
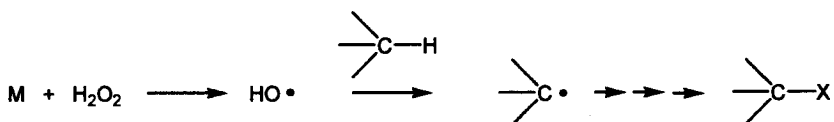
Fortunately, during the last few decades, new systems based on metal complexes have been discovered which allow us to oxidize saturated hydrocarbons under relatively mild conditions, and these reactions are relatively efficient [1]. It is necessary to emphasize, however, that efficiencies of alkane oxygenations are usually noticeably lower in comparison with, for example, olefin epoxidations (which are also often catalyzed with transition metal complexes) or oxidation of alcohols to ketones. An over-oxidation can be avoided if an excess of an alkane over an oxidizing reagent is employed, but in this case the yield of products based on the starting hydrocarbon will be much less than quantitative. Typically, yields of 10–30% based on either a starting alkane or an oxidant can be considered as good. Certain groups connected with methylene fragments of molecules can dramatically enhance the reactivity of C–H bonds. For example, oxygenation of benzylic or allylic positions (activated by aryl or olefin fragments, respectively) or reactions of ethers (activated by alkoxy groups) proceed much more easily than the corresponding oxidations of cyclohexane and especially normal hexane. On the other hand, electron-deficient substituents (–CN, –NO₂, –COOH) make the neighboring CH₂ groups less reactive, and such liquids as acetonitrile, nitromethane, or acetic acid are appropriate solvents for oxidations of alkanes including even methane and ethane.

An important parameter for metal-catalyzed alkane oxidations is turnover number (TON), which is given by the total moles of products produced per mole of a catalyst. In some cases, parameters such as turnover number per hour or minute (turnover frequency, TOF) are used. The TON parameter is more preferable from the “synthetic” point of view because in some cases a very rapid initial reaction (with high TOF in min^{-1} or even in s^{-1}) can soon stop, and the final TON will be quite low. The range of possible solvents for alkane oxidations is very narrow. As mentioned above, usually liquids containing C–H bonds “deactivated” by electron-withdrawing substituents are used as solvents; these are acetic acid, acetonitrile, nitromethane, and methylene chloride. Pyridine (Gif-oxidations) or perfluorinated liquids have been employed in some “exotic” cases. Water – which is resistant to the action of normal oxidants – is a very attractive solvent, but it was used only in the case of lower alkanes (methane and ethane), because they are relatively soluble (under pressure) in aqueous solutions. The same can be said about concentrated sulfuric acid.

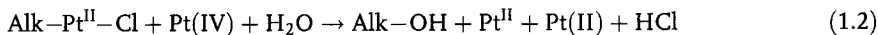
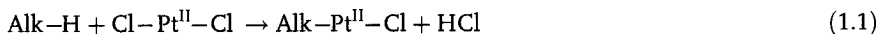
This chapter deals with oxidative activation of C–H bonds in saturated and aromatic hydrocarbons as well as in some other C–H-containing compounds (e.g., in olefins) by metal complexes in solutions under mild conditions (that is at temperatures lower than 100–150°C) with predominant emphasis on synthetic aspects of described reactions. Oxygenations (i.e., insertion of an oxygen atom into the C–H bond) published during last few years are mainly considered; earlier work has been described in books and reviews [1].

From the mechanistic point of view, C–H activation processes can be divided into three types. The first group includes reactions involving “true”, “organometallic” activation of the C–H bond, i.e., reactions where organometallic derivatives (i.e., compounds containing a metal–carbon σ -bond) are formed as an intermediate or as the final product. In the second group, we include reactions in which the contact between the complex and the C–H bond is only via a complex ligand during the process of the C–H bond cleavage. The σ -C–M bond is not generated directly at any stage. In these reactions the function of the metal complex usually consists in abstracting an electron or a hydrogen atom from the hydrocarbon. Finally, in the processes that belong to the third type, a complex activates initially not the hydrocarbon but another reactant (for example, hydrogen peroxide or molecular oxygen). The reactive species formed (for example, hydroxyl radical) then attacks the hydrocarbon molecule without any participation of the metal complex in the latter process. The metal catalyst does not take part in the direct “activation” of the C–H bond by the radical. The hydrocarbon oxidations in living cells under the action of certain metal-containing enzymes proceed as reactions of the second or third type [1]. Although these oxidations occur via the formation of reactive radicals, they are selective and give the products and energy necessary for microorganisms. Biodegradation of hydrocarbons also requires metal-containing enzymes [1]. It is very interesting that microorganisms are known to degrade hydrocarbons under strictly anoxic conditions [2].

Three types of oxidative activation of C–H bonds

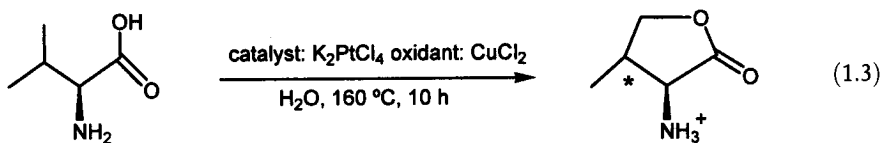
First ("organometallic"):*Second ("via a ligand at M"):**Third ("activation of other reactant"):*

Organometallic stoichiometric and catalytic activation of C–H bonds in alkanes and arenes gives rise to hydrocarbon functionalization (numerous examples can be found in [1 a–d]; see also certain recent publications [3]). Although the mechanisms of the reaction with C–H bonds are in many cases unknown, we can state that metal-catalyzed oxygenations (i.e., processes of oxygen atom insertion) of saturated hydrocarbons rarely begin from the formation of the σ -C–M bond (the first type of activation). An unambiguous example of the organometallic (first type) activation is the Shilov reaction [1, 4], which enables the oxidation of alkanes in aqueous solutions under catalysis by platinum(II) complexes. The first step of the reaction is the formation of a σ -alkyl platinum(II) derivative, which is then oxidized by platinum(IV) present in the solution to give alkanol (and also alkyl chloride):



Since the first step proceeds via a direct contact of the C–H bond with a voluminous Pt^{II} -containing species, the reaction exhibits an "unusual" bond selectivity, i.e. the stronger C–H bonds of methyl groups react faster than the weaker secondary and tertiary C–H bonds: $1^\circ > 2^\circ > 3^\circ$. Hexachloroplatinate, used originally as the stoichiometric oxidant, is obviously a very inconvenient reagent because it is too expensive to be used in the synthesis. In recent years, attempts to employ other cheap oxidants have been made. Sames and co-workers found that salts CuCl_2 and CuBr_2 can regenerate the active platinum species [5 a]. In the L-valine oxida-

tion by the system $\text{K}_2\text{PtCl}_4\text{--CuCl}_2$, TONs attained 20 and isolated yields of lactones were up to 35%.



Interestingly, the C–H bond functionalization occurred with regio- and stereoselectivity; anti and syn lactones were produced in a 3:1 ratio.

Thorn and co-workers used the Pt(II)–Pt(IV)– H_2O_2 system to hydroxylate *n*-propanol selectively to 1,3-propanediol [5 b], but the efficiency was very low: the amount of 1,3-propanediol corresponded to 1.3 turnovers of the entire platinum content (about 0.09 h^{-1}). Periana et al. [5 c] found that platinum complexes derived from the biazine ligand family catalyze the oxidation of methane by sulfuric acid to a methanol derivative, giving a one-pass yield of >70% based on methane. These complexes are very stable in concentrated sulfuric acid at relatively high temperature and are among the most effective catalysts for methane conversion. Under the action of platinum, arenes give biaryl compounds with good yields [1, 5 d].

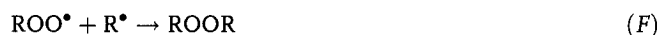
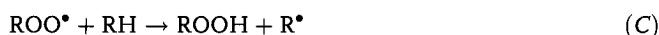
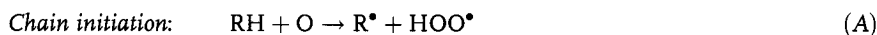
Unlike the reactions mentioned above, almost all processes described in this chapter can be considered to belong to the second and third types of C–H bond activation. From the mechanistic point of view, all hydrocarbon oxidations occurring in living organisms [1, 6 a–c] are also of the second or third types (i.e. they do not involve organometallic activation). However, it has been shown in a recent publication [6 d] that aryl C–H activation occurs in copper complexes with triaza-macrocyclic ligands, which is a model of the hydroxylation performed by a binuclear copper enzyme tyrosinase. The authors noted that “while the generally accepted enzymatic mechanism does not involve direct aryl C–H activation by a Cu^{II} center, no current data precludes it”. Metal complexes that are models of certain metal-containing enzyme centers often efficiently oxygenate saturated and aromatic hydrocarbons. Metal derivatives of porphyrins play an important role in hydrocarbon functionalization [6 e, f], and not only in oxygenation processes [6 g]. Another field which gives models of metal-catalyzed and enzymatic processes (and consequently helps us to understand their mechanisms) is activation of C–H bonds in the gas phase [7]. Finally, metal-catalyzed oxidations of hydrocarbons are processes of great importance both for laboratory and industrial practice [8]. In this chapter we will consider only recent publications devoted to metal-catalyzed liquid-phase reactions. Different sections of the chapter are devoted to functionalization by certain oxidative reagents.

2.2.2

Oxidation with Molecular Oxygen

Doubtless, molecular oxygen (and especially air) is the most cheap, convenient, and green [9] oxidation agent in organic chemistry. Thermodynamically, the formation of oxygen-containing products from saturated hydrocarbons and molecular oxygen is always favorable because oxidation reactions are highly exothermic. The complete oxidation of alkanes by air (burning) to produce water and carbon dioxide is a very important source of energy. There can also be partial oxidation (autoxidation) of saturated hydrocarbons producing various valuable organic substances, e.g., alkyl hydroperoxides, alcohols, and ketones or aldehydes.

Non-catalyzed autoxidation [1 b] of saturated hydrocarbons in the liquid phase is usually a branched-chain process. Hydroperoxides are the intermediates in liquid phase oxidation. Let us consider first the mechanism of non-catalyzed oxidation. The following classical scheme represents the typical mechanism of liquid-phase hydrocarbon oxidation.



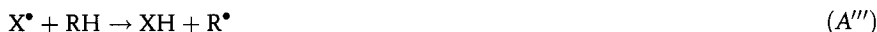
Highly reactive radicals RO^\bullet and HO^\bullet can take part in the following fast steps:



Relatively unstable chemical initiators can be used to initiate the reaction generating alkyl radicals, R^\bullet . For example, in the case of azobis(isobutyronitrile) (AIBN, In-N=N-In) [10 a], the chain initiation step



is much more efficient in comparison with stage (A). An alkane oxidation can be also initiated by any other free radicals, X^\bullet , which are capable of abstracting the hydrogen atom from an alkane:



Very reactive hydroxyl and alkoxy radicals are among potential initiators of alkane oxidations. Often, at low temperature and at least at the beginning of the reaction, the catalyzed oxidation of an alkane, RH, initiated with H_2O_2 or *tert*-BuOOH (see below), gives rise almost exclusively to the corresponding alkyl hydroperoxide, ROOH. This supports the view that chain-branching steps *D* and *D'*, which can give the alcohol in the propagation step *C'''*, are not involved in the alkane hydroperoxidation mechanism.

An important question arises whether the radical-*chain* oxidation of the alkane with molecular oxygen is possible at low temperature or the oxidation reaction occurs as a simple radical-initiated process with the rate less than the initiation rate. The simplified mechanism of an initiated non-branched radical-chain liquid-phase oxidation of a hydrocarbon, RH, can be described by the following equations:



In this scheme, R^\bullet are alkyl radicals, ROO^\bullet are peroxy radicals, Eq. (2.1) corresponds to the stage of radical generation with the rate W_i , Eqs. (2.2) and (2.3) represent the cycle of chain propagation, and Reaction 2.4 is the chain termination step. Reaction (2.3) is the crucial step for the classical radical chain route. Let us assume that at low temperature the sole terminal product of the oxidation is alkyl hydroperoxide, ROOH. The results of the kinetic analysis of the scheme 2.1–2.4 are summarized in Tab. 1 [10b]. It follows from the data of this table that for a hydrocarbon such as cyclohexane, and especially for the much more inert ethane and methane at 30 °C, we have in principle no reason to consider the possibility of the chain process according to scheme 2.1–2.4. Even at 100 °C for the 10% transformation of ethane and methane via mechanism 2.1–2.4, the reactions will take 6.5 and 30 days, respectively, and the highest possible rate of the chain process is extremely low for these hydrocarbons. For hydrocarbons with weak C–H bonds, such as tetralin and cyclohexene (allylic methylenes), as well as cumene, corresponding transformations via route 2.3 will take less than one hour and consequently are quite possible.

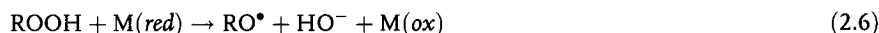
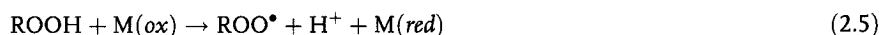
Ions of transition metals are often used in catalytic low-temperature alkane oxidations. While the classical radical-chain mechanism of the alkane oxidation (steps 2.2, 2.3 and 2.4) remains unchanged, catalysts take part in the initiation

Tab. 1 Highest possible rates of the hydrocarbon *radical-chain* low-temperature oxidation and the minimum possible times $\tau_{0.1}^0$ for the transformation of these hydrocarbons to the extent of 10%^{a)}

No.	Hydrocarbon	Rate W_i^{max} ($\text{mol dm}^{-3} \text{s}^{-1}$)		Time $\tau_{0.1}^0$	
		30 °C	100 °C	30 °C	100 °C
1	Tetralin	9.1×10^{-6}	1.0×10^{-4}	1.7 hours	0.2 hours
2	Cyclohexene	6.3×10^{-6}	5.1×10^{-5}	2.5 hours	0.3 hours
3	Ethylbenzene	8.3×10^{-8}	7.3×10^{-6}	7.5 days	2.1 hours
4	Toluene	2.3×10^{-10}	1.0×10^{-7}	7.5 years	6.5 days
5	Cumene	2.0×10^{-6}	1.2×10^{-4}	7.5 hours	0.2 hours
6	Cyclohexane	5.5×10^{-11}	1.0×10^{-7}	32.5 years	6.5 days
7	Ethane	3.2×10^{-12}	1.0×10^{-7}	550 years	6.5 days
8	Methane	7.9×10^{-14}	2.1×10^{-8}	22000 years	30 days

a) The parameters have been calculated assuming a hydrocarbon concentration of 1.0 mol dm^{-3} (although in many cases it is lower).

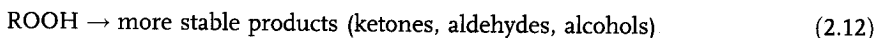
stage, inducing the initiator decomposition to produce free radicals. This case is not different from the initiated alkane oxidation considered above, and here all parameters estimated previously can also be used. On the other hand, complex ions of transition metals could effectively interact with the alkyl hydroperoxide formed in the oxidation process even at relatively low temperature. This interaction results in the peroxide decomposition, generating free radicals. In this case we have to add to the scheme 2.1–2.4 the following stages (M is an ion of transition metal in oxidized or reduced form):



It should be noted that if in the case of mechanism 2.1–2.4 the final product of the reaction is alkyl hydroperoxide, ROOH, the mechanism 2.5–2.7, which is a branching one, gives rise to the alcohol as a main product. The analysis in steady-state approximation of the kinetic scheme taking into account 2.5–2.7 leads us to the conclusion that the rate of the ROOH decomposition with participation of a catalyst is only 1.5 times higher than the rate of hydrocarbon consumption in the chain termination step. In the latter case the composition of the products can be dramatically changed. Since in some metal-catalyzed oxidations, at least at low (<50 °C) temperatures and at least at the beginning of the reaction, cyclohexane and normal alkanes are transformed only into alkyl hydroperoxides, we can disregard a mechanism involving steps 2.5–2.7. Taking this into account, we conclude that, in accordance with data summarized in Tab. 1, the classical radical-chain

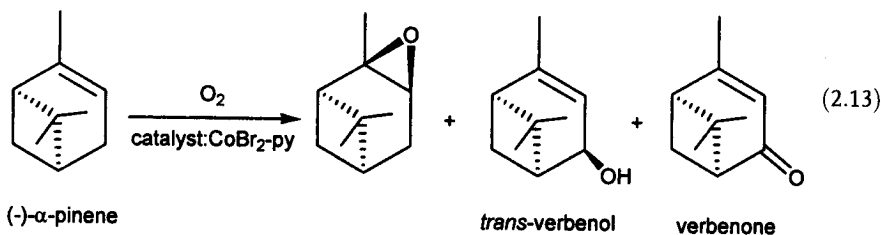
mechanism 2.1–2.4 should be neglected for this case. However, the increment of this pathway might be expected for easily oxidizable hydrocarbons such as tetralin, cyclohexene, etc.

It should be emphasized that the analysis described above does not exclude the possibility of the oxidation of cyclohexane, methane, and other alkanes having strong C–H bonds at a high rate via a radical *non-chain* mechanism, for example, according to the third type of C–H bond activation:



It can be seen, however, that in this case an oxidizing system requires a source of stoichiometric amounts of radicals initiating the oxidation.

In practice, autoxidation of C–H compounds is usually carried out in the presence of various metal complexes, and its mechanism involves reaction 2.6 as a crucial step (Haber-Weiss decomposition of hydroperoxides). Radicals RO^\bullet are more reactive in comparison with ROO^\bullet , which makes possible the chain mechanism via step 2.7. The reactions occur typically at temperatures around 100°C without solvents, in the presence of surfactants or in inert solvents (e.g., acetic acid). Only compounds containing relatively weak C–H bonds can be oxidized: alkylbenzenes, olefins into allylic position, high branched and normal alkanes. Some examples of these oxidations are presented in Tab. 2. Alkyl hydroperoxides and/or alcohols and ketones are the products of these reactions. In some cases alkyl chain dehydrogenation occurs. The oxidation of (–)- α -pinene catalyzed by the cobalt derivative gave verbenone with good yield [11 n]:



The system consisting of cobalt or manganese acetate and sodium bromide catalyzes a very efficient autoxidation of methylarenes to corresponding arenecarboxylic acids in acetic acid (cobalt-bromide catalysis, which is the basis for the industrial MC/Amoco process) [12 a]. Saturated hydrocarbons cannot be oxidized by this method. Branched hydrocarbons (isobutane) and even cycloalkanes (cyclooc-

Tab. 2 Autoxidation of hydrocarbons with relatively weak C–H bonds in the presence of metal complexes

No.	Hydrocarbons	Catalysts	Ref.
1	Ethylbenzene	Nickel bis(acetylacetonate) and nickel bis(enaminoacetonate)	11 a
2	Cumene	Transition metal salts supported on polymer	11 b
3	<i>p</i> -Xylene ^{a)}	MnBr ₂	11 c
4	Alkylaromatics ^{b)}	[H ₂ F ₆ NaV ^W W ₁₇ O ₅₆] ⁸⁻	11 d
5	Adamantane and 1,3-dimethyladamantane ^{b)}	K ₅ FeSi(OH ₂)W ₁₁ O ₃₉ · 3H ₂ O and Na ₆ MnSi(OH ₂)W ₁₁ O ₃₉ supported on Al ₂ O ₃	11 e
6	Ethylbenzene	Cobalt bis(acetylacetonate), cationic surfactant	11 f
7	1-Hexene ^{c)}	[Ir(CH ₃ CN) ₄ NO ₂] ²⁺	11 g
8	Cyclohexene	Vanadyl Schiff base complexes	11 h, i
9	Cyclohexene, tetralin	VO(acac) ₂	11 j
10	Cyclohexene	Bimetallic Pd(II) complex	11 k
11	Tetrahydrofuran ^{d)}	Mo/Ru complexes	11 l
12	Isochroman ^{e)}	Multi-Cu oxidase laccase	11 m

a) Selective oxidation to terephthalic acid in supercritical H₂O at ca. 400 °C.

b) Simultaneous oxygenation and oxydehydrogenation.

c) Conversion 79%, products: 1,2-epoxyhexane (24), 1-hexen-3-one (26), 2-hexenal (20), 1-hexen-3-ol (5), 2-hexen-1-ol (3).

d) The oxidation catalyzed with [Ru(CO)₂Cp]₂ gave γ -butyrolactone (TON=290) as well as propylformate (TON=48).

e) Corresponding lactone was obtained with yield 10% in the oxidation in the presence by TEMPO (2,2',6,6'-tetramethylpiperidine-*N*-oxide).

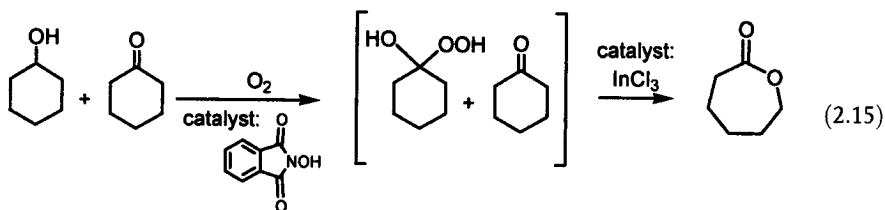
tane) can be efficiently oxygenated with molecular oxygen under catalysis with certain metal porphyrins and some other complexes (Lyons system) [12b–d].

Ishii and coworkers described the oxidation of organic compounds including alkanes by molecular oxygen catalyzed by *N*-hydroxyphthalimide (NHPI) combined with Co(acac)_{*n*} (*n*=2, 3) or transition metal salts [12e]. The analogous system “NHPI–ammonium hexanitratocerate(IV)” enables C–H bonds to be functionalized under argon atmosphere [12f]:



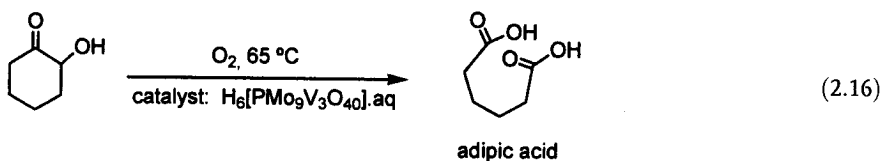
Metal complexes also catalyze the hydroxylation of aromatics with molecular oxygen. Thus, heteropolyacid H₆PMo₉V₃O₄₀ encapsulated in mesoporous MCM-41 and microporous VPI-5 molecular sieves catalyzes the transformation of benzene to phenol with a TON of 800 [12g].

Catalytic splitting of C–C bonds in alcohols and ketones occurs with simultaneous cleavage of C–H bonds. For example, treatment of a mixture of cyclohexanone and cyclohexanone (KA-oil, a very important intermediate for the production of nylon) by the Ishii oxidation system gives rise to the BaeyerVilliger products [12h]:



It has recently been shown by Sheldon and co-workers that NHPI, in the absence of any metal complex, catalyzes the selective oxidation of cyclohexylbenzene to cyclohexylbenzene-1-hydroperoxide [12 i]. This reaction provides the basis for a new coproduct-free route to phenol.

Deep catalytic oxidation of cyclohexanone derivatives (as well as other ketones) [12 j-] affords corresponding acids, for example [12 l]:



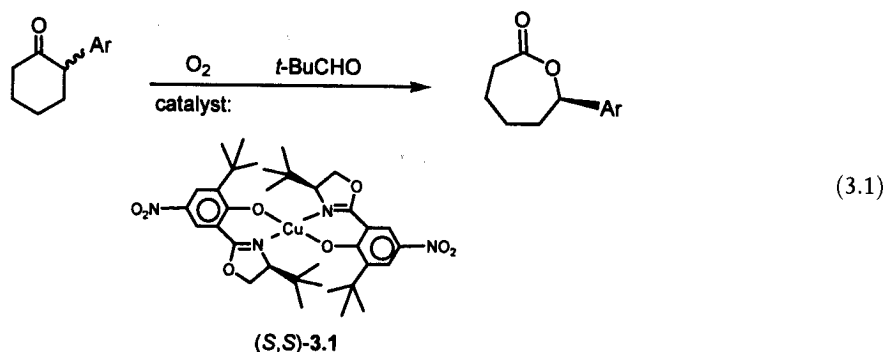
This reaction is reminiscent of biological oxidations catalyzed by catechol dioxygenases [12 k, m].

2.2.3

Combination of Molecular Oxygen with a Reducing Agent

Unlike the case of dioxygenases, which insert both atoms from the O_2 molecule into the substrate, the biological oxidation of hydrocarbons catalyzed by monooxygenases is coupled with the oxidation of electron donors, such as NADH or NADPH. The donor in biological oxidation is believed to transfer its electrons initially to the metal ion, which is subsequently oxidized by an oxygen molecule. It should be noted that hydrocarbons could play the role of reductants, although it is very difficult to abstract proton or hydrogen from these compounds. Some chemical systems based on metal complexes and involving molecular oxygen as the oxidant require a reducing agent which can easily provide the system either with electron or with hydrogen atom. Tab. 3 summarizes examples of the aerobic oxidations with participation of a reductant.

Copper complex 3.1 in the presence of pivaldehyde catalyzes aerobic oxidation of racemic 2-arylcylohexanones to afford the corresponding lactones with enantioselectivities of up to 69% *ee* [13 o]:



Tab. 3 Autoxidation of hydrocarbons in the presence of reducing agents

No.	Hydrocarbons	Catalysts	Reductant	Efficiency	Ref.
1	Cyclohexane ^{a)}	FeCl ₃ -picolinic acid	H ₂ S	Conversion 36%	13a
2	Alkanes	Copper salts	Aldehydes	Yield 4.3% (on converted cyclohexane)	13b
3	Adamantane and alkylaromatics	Metal acetylacetonates	3-Methylpropanal	Conversion of adamantane 81%	13c
4	Cyclohexane, <i>n</i> -hexane	Immobilized Fe carboxylate complex	Mercaptane, PPh ₃	Yield TON=119	13d
5	Methane ^{c)}	V complexes	Zn/CF ₃ CO ₂ H	TON=11	13e
6	Indane copper derivatives		Isobutyraldehyde	Conversion 49%	13f
7	Cyclohexane	Porphyrinato-iron(III)	Ascorbic acid	TON=17	13g
8	Adamantane	Fe oxo/peroxo pivalate	Zn/Pivalic acid	Low product yield	13h
9	Methane	Pd/C + Cu(MeCO ₂) ₂	H ₂	TON=13	13i
10	Cyclooctane	NaAuCl ₄	Zn/CH ₃ CO ₂ H	TON=10	13j
11	Cyclooctane ^{d)}	No catalyst	Acetaldehyde	Yield 22%	13k
12	Benzene cyclohexane	Pd/Al ₂ O ₃ + V or Fe	H ₂	TOF up to 59 h ⁻¹	13l
13	Benzene	Pt/SiO ₂ + V(acac) ₃	H ₂		13m
14	Benzene ^{e)} cyclohexane	VO ₃	Ascorbic acid, Zn/CH ₃ CO ₂ H	TON up to 78	13n

a) Under Gif conditions, i.e. in MeCN in the presence of 4-*tert*-butylpyridine.

b) In the presence of *t*-butyl hydroperoxide.

c) In CF₃CO₂H.

d) In the presence of compressed carbon dioxide at 42–90°C. Predominant formation of cyclooctanone.

e) The oxidation occurs in acetonitrile only in the presence of pyridine, pyrazinic acid, and acetic acid; no reaction if ascorbic acid is dissolved in the reaction medium.

In concluding the two first sections, we can state that in the aerobic oxidation two mechanistic pathways lead to the C–H activations. These can be conventionally called the “dioxygenase” route (insertion of both oxygen atoms from the O₂ molecule) and the “monooxygenase” route (insertion of only one oxygen from the O₂ while the second oxygen is reduced to water by a reductant). Obviously, the dioxygenase type is more profitable from the practical point of view, because the monooxygenase type requires “non-productive” use of a reducing agent (and also “non-productive” use of half of the oxygen, which is not so important because air is a very cheap reagent). The dioxygenase type can be successfully used for the oxidation of compounds with C–H and C–C bonds activated by neighboring oxo or hydroxy groups. An example is shown in Eq. (2.16). As stated above, the radical-chain oxidation of saturated hydrocarbons under mild conditions is possible only in the case of compounds containing relatively weak C–H bonds. Usually this process is non-selective and gives many products. The monooxygenase route is much more selective: hydroxylation of even lower alkanes can be carried out at room temperature like biological oxidations (methane monooxygenase [1, 6b], cytochrome P450 [1, 13p]). A very important variant of this route is the use of oxidants containing oxygen in a “reduced form”. These are called “oxygen atom donors”. The next sections are devoted to oxidations by oxygen atom donors.

2.2.4

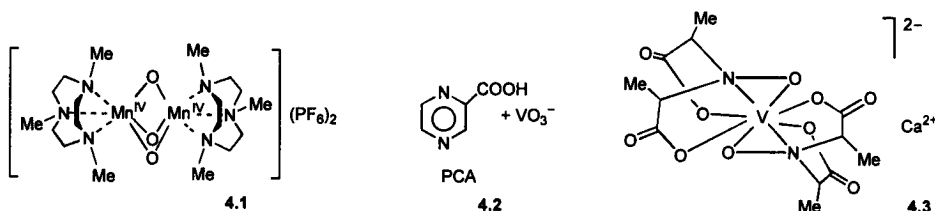
Hydrogen Peroxide as a Green Oxidant

Hydrogen peroxide is a very convenient oxidant and also the cheapest (after molecular oxygen and air). Moreover, like dioxygen, it is a “green” reagent because water is the only by-product in these oxidations [14a]. It can be used in laboratory practice and also in industrial production of relatively expensive products (for the large-scale production of simple alcohols from alkanes, hydrogen peroxide would appear to be too expensive).

In the absence of catalysts under mild conditions (low temperatures, usual solvents) hydrogen peroxide does not react even with compounds containing weak C–H bonds. Certain metal complexes catalyze not only the “non-productive” decomposition of H₂O₂ to H₂O and O₂ but also alkane oxygenation. Corresponding alkyl hydroperoxides are usually formed, at least at the beginning of the reaction. Alkyl hydroperoxides formed in H₂O₂ oxidations can be determined quantitatively if the solution samples are injected into the GC equipment before and after treatment with triphenylphosphine [1b, d, 14b].

One of the most efficient systems for alkane oxidation, proposed recently, is based on the dinuclear manganese(IV) derivative [L₂Mn₂O₃](PF₆)₂ (**4.1**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). Complex **4.1** catalyzes very efficient oxygenation of various organic compounds in acetonitrile or nitromethane only if a carboxylic acid is present in small concentration in the reaction mixture [15a, b]. Light (*n*-methane, ethane, propane, normal butane, and isobutane) and higher (*n*-hexane and *n*-heptane, decalin, cyclohexane, methylcyclohexane, etc.) alkanes can

easily be oxidized by the “H₂O₂–4.1–CH₃CO₂H” system at room temperature, at 0°C, and even at –22°C. Turnover numbers of 3300 have been attained after 1–2 h, and the yield of oxygenated products was 46% based on the alkane. The oxidation initially affords the corresponding alkyl hydroperoxide as the predominant product. However, this compound decomposes in the course of the reaction to produce the corresponding ketone and alcohol.



Regio and bond selectivities of the reaction are high: C(1):C(2):C(3):C(4) \approx 1:40:35:35 and 1°:2°:3° is 1:(15–40):(180–300). The reaction with *cis*- or *trans*-isomers of decalin gives (after treatment with PPh₃) alcohols hydroxylated in the tertiary position with a *cis/trans* ratio of \sim 2 in the case of *cis*-decalin and a *trans/cis* ratio of \sim 30 in the case of *trans*-decalin. It has been proposed [15b] that catalytically active species containing an Mn^{III}Mn^{IV} fragment is formed in the solution. The alkane oxidation begins with hydrogen atom abstraction from the alkane by oxygen-centered radical or radical-like species. The active oxidant is probably a dinuclear manganese complex (HOO–)MnMn(=O), and the reaction occurs via an “oxygen-rebound mechanism” between radical R[•] and the HOO– group to produce ROOH with retention of stereochemistry. Alkyl radicals (R[•]) can also partially escape from the solvent cage and react with dioxygen to generate ROO[•] and subsequently ROOH with some loss of stereochemistry.

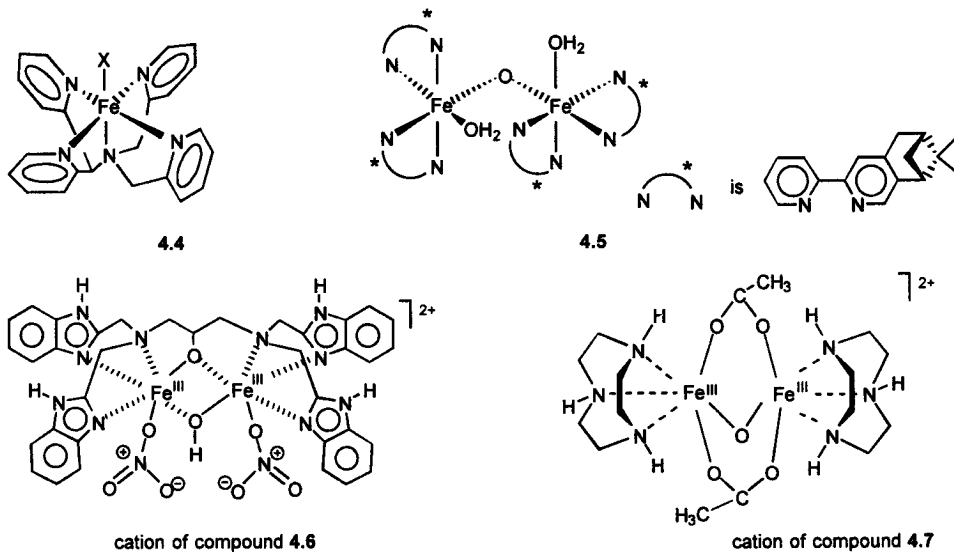
The soluble manganese(IV) complex containing as ligands 1,4,7-triazacyclononane moieties bound to a polymeric chain also catalyzes oxidation of alkanes, and the presence of relatively small amount of acetic acid is obligatory for this reaction [15c]. It is interesting that the oxidation of alkanes and olefins exhibits some features (kinetic isotope effect, bond selectivities) that distinguish this system from an analogous system based on dinuclear Mn(IV) complex 4.1. A combination of MnSO₄ and 1,4,7-trimethyl-1,4,7-triazacyclononane in the presence of oxalate, ascorbate, or citrate buffers catalyzes the oxidation of arylalkanes with hydrogen peroxide [15d]. Ethylbenzene was oxidized at 40°C with TOF = 188 h^{–1}.

Any soluble vanadium derivative, for example ⁿBu₄NVO₃, VOSO₄, VO(acac)₂, can be used as a catalyst in combination with pyrazine-2-carboxylic acid (PCA) as co-catalyst (combination 4.2) for the oxidations with hydrogen peroxide in acetonitrile solution [16]. At low temperatures, the predominant product of alkane oxidation is the corresponding alkyl hydroperoxide, while alcohols and ketones or aldehydes are formed simultaneously in smaller amounts. This alkyl hydroperoxide then slowly decomposes to produce the corresponding ketone and alcohol. Atmospheric oxygen takes part in this reaction; in the absence of air the oxygenation reaction does not proceed. Thus, in alkane oxidation, hydrogen peroxide plays the

role of a promoter while atmospheric oxygen is the true oxidant. The oxidation of *n*-heptane by the reagent under consideration exhibits low selectivity: C(1):C(2):C(3):C(4) \approx 1:4:4:4. Methane, ethane, propane, *n*-butane, and isobutane can also be readily oxidized in acetonitrile by the same reagent. In addition to the primary oxidation products (alkyl hydroperoxides), alcohols, aldehydes or ketones, and carboxylic acids are obtained with high total turnover numbers (at 75 °C after 4 h: 420 for methane and 2130 for ethane) and H₂O₂ efficiency. Methane can also be oxidized in aqueous solution, giving in this case methanol as the product (after 20 h at 20 °C the turnover number is 250). The reagent also oxygenates arenes to phenols and alcohols to ketones, and hydroperoxidizes the allylic position in olefins. The crucial step of the oxidation by the reagent “O₂–H₂O₂–VO₃[–] – pyrazine-2-carboxylic acid” is the very efficient generation of HO[•] radicals. These radicals abstract a hydrogen atom from the alkane, RH, to generate the alkyl radical, R[•]. The latter reacts rapidly with an O₂ molecule affording the peroxy radical, ROO[•], which is then transformed simultaneously into three products: alkyl hydroperoxide, ketone, and alcohol. The proposed mechanism of HO[•] generation involves the reduction of V(V) species by the first molecule of H₂O₂ to give a V(IV) derivative. No oxidation occurs in the absence of pyrazine-2-carboxylic acid. The possible role of pyrazine-2-carboxylic acid is its participation (in the form of a ligand at the vanadium center) in the proton transfer, which gives the hydroperoxy derivative of vanadium.

Zeolite-encapsulated vanadium complexes with picolinic acid are also efficient (although less so) in hydrocarbon oxidations [17a, b]. Synthetic amavadine (present in *Amanita* fungi) models, for example, complex 4.3, exhibits haloperoxidase activity and catalyzes [17c] in the presence of HNO₃ oxo-functionalization of alkanes and aromatics with TONs up to 10. Alkanes can be oxidized by hydrogen peroxide using vanadium-containing polyphosphomolybdate [PMo₁₁VO₄₀]^{4–} as catalyst in acetonitrile [17d] or trifluoroacetic anhydride [17e, f]. Complex K_{0.5}(NH₄)_{5.5}[MnMo₉O₃₂] is a catalyst for phenol hydroxylation with 30% H₂O₂ in methanol [17g].

Mono- and dinuclear iron complexes with various *N*-containing ligands are good catalysts for the H₂O₂ oxidations of hydrocarbons. These complexes, for example 4.4 [18a–c], 4.5 [18d], 4.6 [18e], and 4.7 [18f] mimic non-heme enzymes (see also certain recent publications [18g, h]). In alkane oxidations, the TONs vary from 2–5 to 100–150. In some cases (complexes like 4.4, chiral complex 4.5), the reaction proceeds stereospecifically; the hydroxylation with complex 4.5 is partially enantioselective. The reactions in acetonitrile catalyzed by compounds 4.6 and 4.7 can be dramatically accelerated by adding picolinic acid or PCA.



Oxidations catalyzed by metalloporphyrins [19] can be considered as models of biological processes occurring under the action of cytochrome P450 and some other heme enzymes [1]. Some other hydrogen peroxide oxidations that are catalyzed by synthetically prepared soluble metal complexes, solid compounds, and even enzymes are summarized in Tab. 4.

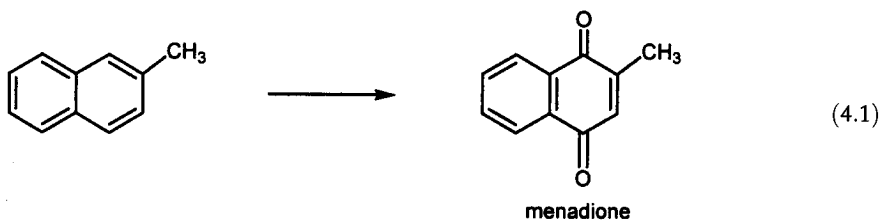
Tab. 4 Examples of catalytic H_2O_2 oxidations of hydrocarbons

No.	Hydrocarbons	Catalysts	Solvent	Efficiency	Ref.
1	Methylbenzenes	$\text{MoO}(\text{O}_2)(\text{QO})_2^{\text{a}}$	Acetonitrile	Yields up to 95% based on substrate	20a
2	Alkanes	Fe derivatives	py/AcOH ^b	TONs 2–30	20b
3	Alkanes	NaAuCl_4 , ClAuPPh_3	Acetonitrile	TON = 520	13j
4	Ethane and other alkanes	CrO_3	Acetonitrile	TON = 620 for the case of ethane	20c
5	Methane, ethane and other alkanes	OsCl_3	Acetonitrile	TON = 102 for ethane, 150 for propane	20d
6	Alkanes	$\text{Ni}(\text{ClO}_4)_2\text{-TMTACN}$	Acetonitrile	TON = 66	20e
7	Alkanes	H_2PtCl_6	Acetonitrile	TON = 44	20e
8	Toluene	Peroxidase	Water		20f

a) QOH is 8-quinolinol.

b) Gif systems. For Gif chemistry see [1, 20g].

Metal complexes also catalyze the oxidation of arenes to phenols or quinones [21]. Methyltrioxorhenium [22a] and Ti- and Fe-containing zeolites [22 b] are catalysts for the practically important oxidation of methyl-naphthalene to menadione (vitamin K₃):

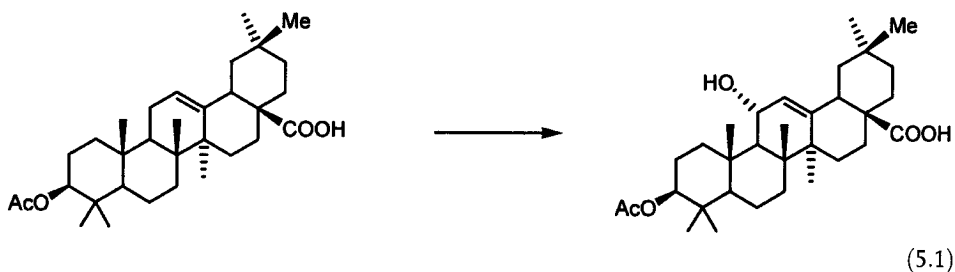


It has recently been shown that the oxidation in acetic acid occurs without any catalyst [22 c].

2.2.5 Organic Peroxy Acids

Peracetic acid oxidizes hydrocarbons if Ru/C [23 a], Ti-containing zeolite [23 b], and manganese-porphyrins [23 c] are used as catalysts. Copper salts, for example, Cu(ClO₄)₂ and some complexes, particularly Cu(CH₃CN)₄BF₄, taken in small concentrations (for example, 10⁻⁵ mol dm⁻³) are also efficient in alkane oxidations with peroxyacetic acid in acetonitrile solution at 60 °C [24 a]. The reaction gives rise to the formation of alkyl hydroperoxides as main products and occurs with low bond selectivity. Total turnover number attains 1900. Various vanadium complexes (particularly, *n*-Bu₄NVO₃) catalyze alkane oxidations by peroxyacetic acid in acetonitrile at 60 °C [24 b]. The reaction gives a mixture of corresponding ketones, alcohols, and alkylacetates; formation of alkyl hydroperoxides can be detected (by reduction with triphenylphosphine) only at the beginning of the reaction. Bond selectivities of the oxidation are not high, which testifies to the formation of free radicals. Analogous “modeling” reactions with H₂O₂ in acetonitrile in the presence of acetic acid or in pure acetic acid gave alkyl hydroperoxides as main products.

Copper(I) complexes catalyze allylic oxidations by *tert*-butylperbenzoate [24 c-f]. Metal-porphyrins [25 a, b] and metal (Mn, Fe, Co) perchlorates [25 c] are good catalysts for C-H oxidations with *meta*-chloroperbenzoic acid, for example [25 a]:

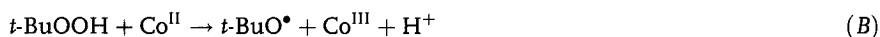
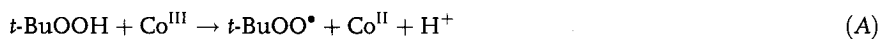


It is interesting that peroxy acids can oxidize alkanes even in the absence of metal catalysts [25 d, e]. Finally, manganese derivative 4.1 catalyzes efficient alkane oxidation with peroxyacetic and *meta*-chloroperbenzoic acids [25 f].

2.2.6

Alkyl Hydroperoxides as Oxidants

Recent examples of hydrocarbon oxidations with alkyl hydroperoxide (usually, *tert*-butylhydroperoxide) are listed in Tab. 5. As Meunier wrote [26 v], “many hydroxylation reactions with alkyl hydroperoxides in the presence of transition-metal complexes are not due to a metal-centered active species, but to a free-radical process initiated by RO[•]”. Alkyl hydroperoxide can act as a radical initiator and as a source of molecular oxygen [26 t]. For example, the oxidation of cyclohexane, CyH, in the presence of cobalt compounds includes the following stages:



2.2.7

Oxidation with Sulfur-containing Peroxides

Bagrii and co-workers [27 a] described oxidation of 1,3-dimethyladamantane and cyclooctane with potassium permonosulfate. Manganese and iron complexes of alkylated tetrapyridylporphyrin were used as catalysts. The latter was either dissolved in a reaction medium or adsorbed on a layered aluminosilicate [27 a]. Tab. 6 shows some other recent examples of metal-catalyzed hydrocarbon oxidations with permonosulfate, HSO₅⁻. This anion can be used either as Oxone[®] (KHSO₄/K₂SO₄/2KHSO₅) in a biphasic solvent containing water and an organic liquid or as an organic-soluble salt, for example, Ph₄PHSO₅.

Fujiwara and co-workers used K₂S₂O₈ as oxidant in various Pd-catalyzed C–H activation processes [3 b, c, 28]. For example, benzene, toluene and other aromatic hydrocarbons can be carboxylated by Pd(II) acetate catalyst with CO in trifluoroacetic acid at room temperature to give the aromatic carboxylic acids [28 b].

Tab. 5 Hydrocarbon oxidation with *tert*-butyl hydroperoxide

No.	Hydrocarbons	Catalysts	Solvent	Efficiency	Ref.
1	Benzylic and allylic C–H	CuCl ₂	CH ₂ Cl ₂ , phase-transfer catalyst	Conversion up to 96%, selectivity 100%	26 a
2	Cyclohexane	Fe(III) and Cu(II) complexes	None	Conversion 4–5%, TON = 70–90	26 b
3	<i>p</i> -Xylene	Zeolite-encapsulated Co and Mn complexes	None	Conversion up to 60%	26 c
4	Alkanes	[Fe ₂ O(η ¹ -H ₂ O)(η ¹ -OAc)(TPA) ₂] ^{3+ a)}	Water	TON = 238 for cyclohexane	26 d
5	Cyclohexane	μ-Hydroxo diiron(II) with L ^{b)}	Acetonitrile	Yield up to 46% based on oxidant	26 e
6	Alkylaromatics	Silicate xerogels containing Co	None	Acetophenone from ethyl-benzene: conversion 65%, selectivity >99%	26 f
7	Ethylbenzene	Cu(I) complexes	MeCN/py	TON up to 34	26 g
8	Alkanes	Ru oxo complexes	Acetone	Yield up to 89% (ethylbenzene)	26 h
9	Pinane	Encaged metal phthalocyanines in Y zeolites	Acetone/ <i>t</i> -BuOH	Conversion 80%, selectivity 90%	26 i
10	Cyclohexane	Ru(III) complex	CH ₂ Cl ₂	Yield up to 38% based on oxidant consumed	26 j
11	Steroids	Co acetate	Acetonitrile	Yield up to 86%	26 k
12	Alkanes, alkylaromatics	Dimanganese(III) complex	CH ₂ Cl ₂	Yield 4.1% (cyclohexane), 4.4% (toluene)	26 l
13	Benzene	Ru(III) complex	CH ₂ Cl ₂	TON = 890	26 m
14	Alkanes	Compound 4.1	Acetonitrile	TON up to 2000	15 a, 26 n
15	Isopropyl arenes	Cu salt-crown ether	None	Yield up to 82%	26 o
16	Toluene, propylbenzene etc.	Mn(II) complexes	CH ₂ Cl ₂	Isolated yield >85%	26 p
17	Unsaturated steroids	Immobilized Co(II), Cu(II), Mn(II), V(II) complexes			26 q
18	Toluene, cyclohexane	Mn ₄ O ₄₆ + cubane complexes	None	TON = 7 (cyclohexane), 101 (toluene)	26 r
19	Cyclohexane	Phthalocyanine Fe(II)	Water/methanol	Yield 8.6%	26 s
20	Cyclohexane	Immobilized Co acetate oligomers	None	Yield up to 3%	26 t
21	Alkanes	Vanadium complexes	Acetonitrile	TONs up to 250 (cyclohexane)	26 u
22	Alkanes	Cu(I) and Cu(II) complexes	Acetonitrile	TONs up to 2000 (cyclohexane)	24 a

a) TPA is tris[(2-pyridil)methyl]amine.

b) L is 1,4,10,13-tetrakis(2-pyridyl)methyl-1,4,10,13-tetraaza-7,16-dioxacyclooctadecane.

Tab. 6 Examples of catalytic oxidations of hydrocarbons with permonosulfate

No.	Hydrocarbons	Catalysts	Solvent	Efficiency	Ref.
1	Ethylbenzene	Mn(III) porphyrins	Dichloroethane	Yields up to 86%	27 b
2	Cycloalkanes	Mn(III) porphyrins	Two-phase ^{a)}	Yield 43% (cyclohexane)	27 c
3	Cyclohexane ^{b)}	Metal sulfo- phthalocyanines	Two-phase	Yields up to 100%	27 d
4	Cyclooctane	Mn tetraphenyl- porphyrin	CH ₂ Cl ₂	Yield 12% (cyclooctane)	27 e

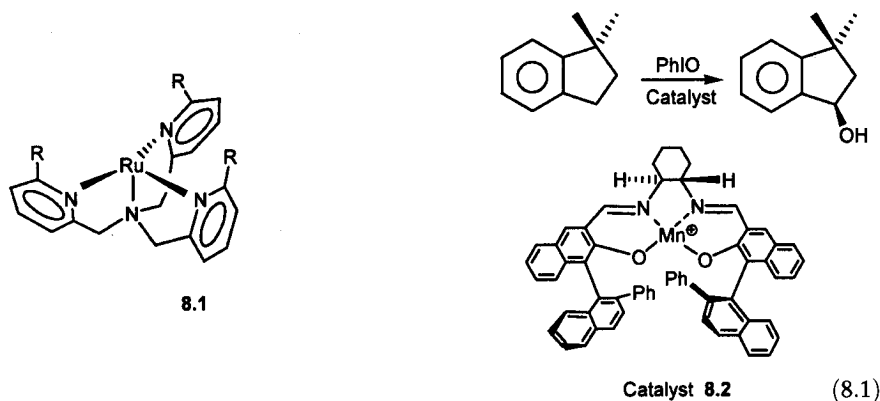
a) Solid Oxone[®]/dichloroethane in the presence of a phase transfer reagent.

b) Oxidation to adipic acid.

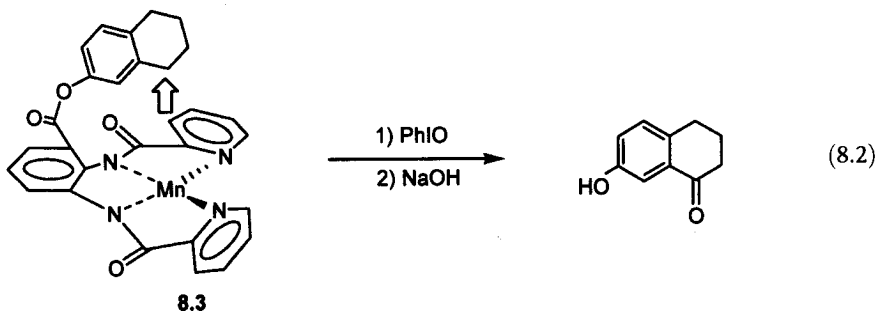
2.2.8

Iodosobenzene as an Oxidant

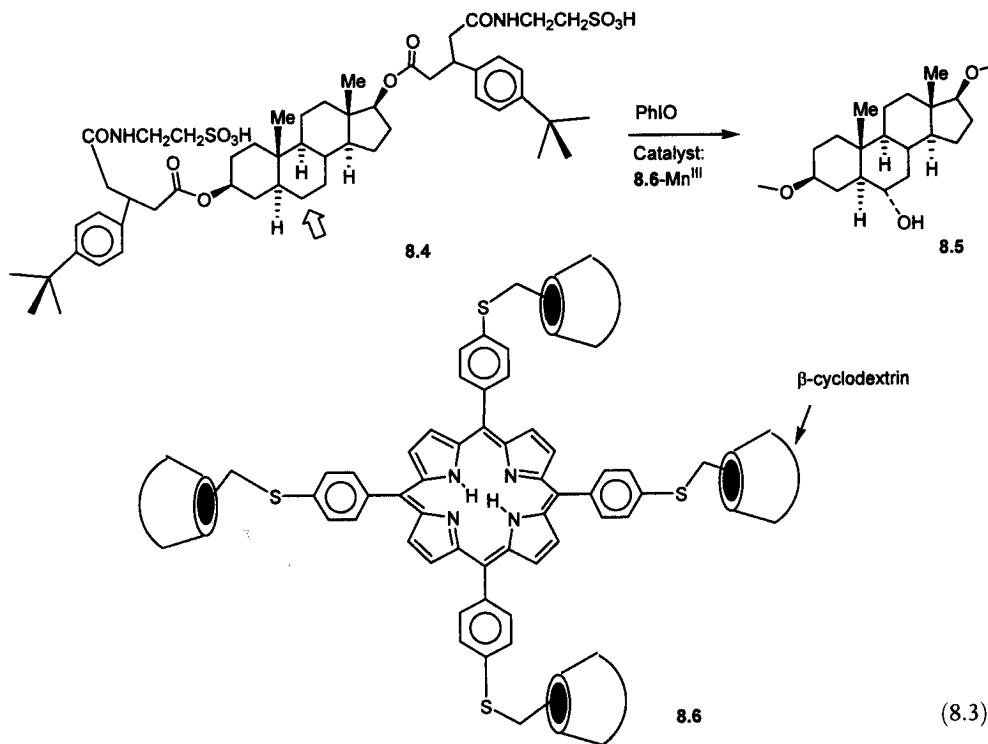
Iodosobenzene, PhIO, is widely used in metal-catalyzed oxidations of various hydrocarbons (Tab. 7). Jitsukawa et al. [30a] found that the catalytic activities of the ruthenium complexes **8.1** containing different substituents at the pyridine 6-position can be fine-tuned. Complexes containing electron-withdrawing groups (for example, R=*t*-BuCONH) promote the epoxidation of cyclohexene, whereas those containing electron-releasing groups (for example, R=*t*-BuCH₂NH) promote mainly the adamantane hydroxylation.



Hydroxylations with iodosobenzene often proceed selectively. Thus, oxidation (Reaction 8.1) of 1,1-dimethylindane catalyzed by optically active manganese complex **8.2** gives the corresponding alcohol with *ee* up to 60% and yield 10% [30 b]. Sames and co-workers were able to ketonize exclusively one benzylic position of the 5,6,7,8-tetrahydro-2-naphthol covalently bound to a metal catalyst center **8.3** [30 c].



Selective hydroxylations of steroids with artificial cytochrome P450 enzymes have been carried out by Breslow and co-workers [30d, e], e.g., hydroxylation of ester derivative **8.4** of androstan-3,17-diol to alcohol **8.5** catalyzed by the Mn(III) complex of porphyrin **8.6** [30e].

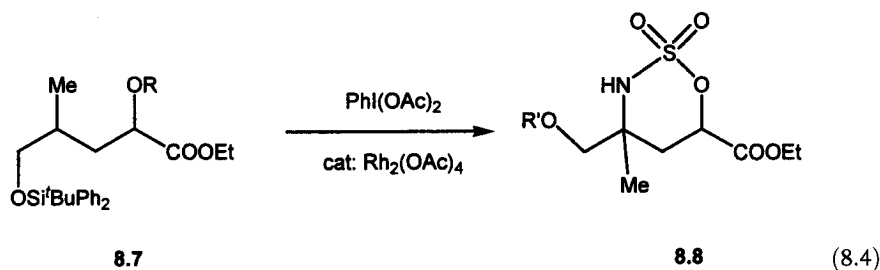


In the synthesis of bromopyrrole alkaloids, When and Du Bois [30f] employed as one of the steps oxidative cyclization of compound **8.7**, which, under the action of $\text{PhI}(\text{OAc})_2$ in the presence of rhodium catalyst, gave smoothly and stereospecifically the oxathiazinane product **8.8**.

Tab. 7 Examples of oxidations of hydrocarbons with iodosobenzene catalyzed by metalloporphyrins

No.	Hydrocarbons	Catalysts	Solvent	Efficiency	Ref.
1	Ethylbenzene	Fe(III) porphyrins	Benzene cyclohexane	Yields up to 73% (cyclohexane, based on PhIO)	29 a
2	Cyclohexane	Acetylglycosylated Fe-, Mn-porphyrins		TONs up to 11	29 b
3	Cyclohexane, adamantane	Homogeneous and supported Mn(III) porphyrins	CH_2Cl_2 ^{a)}	Yields up to 44% (cyclohexane, based on PhIO)	29 c
4	Cyclohexane	Sterically hindered Fe(III) porphyrins	None	Yields up to 72%	29 d
5	Cyclohexane	Mn(III) porphyrins	Dichloroethane	Yields up to 92%	29 e
6	2-Methylbutane	μ -Oxo-bimetallo-porphyrins	Chlorobenzene	Yields up to 7%, based on PhIO	29 f

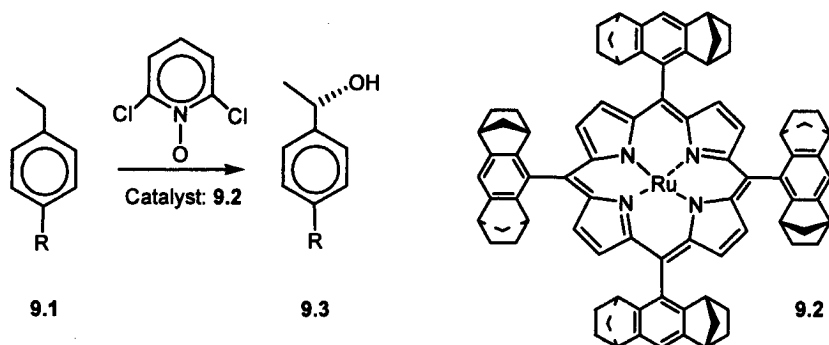
a) In the presence of co-catalysts (pyridine, imidazole).



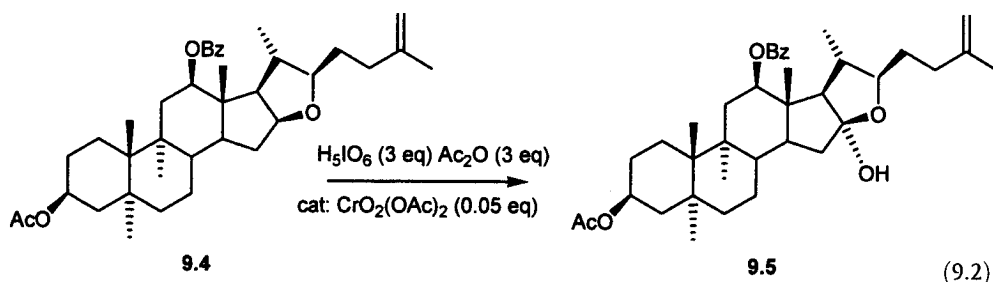
2.2.9

Oxidations with Other Reagents

In recent years, various oxidants have been employed that are less common in comparison with hydrogen peroxide and alkyl hydroperoxides. Some of them cannot be considered as "green" reagents, for example, hypochlorite. Selected examples of such oxidations are summarized in Tab. 8. The oxidation of ethylbenzenes 9.1 with 2,6-dichloropyridine *N*-oxide (proposed earlier by Higuchi and co-workers [32a]), catalyzed by porphyrin 9.2, gave corresponding alcohols 9.3 with *ee* up to 75% [32b].



Lee and Fuchs [32 c] described very recently an unprecedented Cr-catalyzed chemoselective oxidation by H_5IO_6 of compound 9.4 to the corresponding hemiacetal 9.5. The reaction proceeds at very low temperature (-40°C) and gives the product in 69% yield.



Tab. 8 Examples of oxidations of hydrocarbons with various oxidants

No.	Hydrocarbons	Oxidant	Catalyst	Efficiency	Ref.
1	Xylenes	Hypochlorite	RuCl_3	Yield 98% (4-chloro-2-methylbenzoic acid)	31 a
2	1,4-Dimethyl cyclohexane	Perchloric acid	Polyphenylferrosiloxane		31 b
3	Polycondensed aromatics	NaBrO_3	Nafion–Ce(IV) and Nafion–Cr(III)	Yields up to 95%	31 c
4	Cycloalkanes, arylalkanes	NaIO_4	Supported Mn(III) complexes	Yields up to 60%	31 d
5	Arenes	H_5IO_6	CrO_3	Yields up to 90%	31 e
6	Limonene	CuCl_2	PdCl_2	Conversion up to 92%	31 f
7	Alkylarenes	PMSO^{a}	$[\text{PMo}_{12}\text{O}_{40}]^{3-}$	TON=300 (anthracene)	31 g
8	NBMA	TMAO ^b	Cu(II) complexes	Yields up to 98%	31 h

a) Phenylmethylsulfoxide.

b) *N*-Benzoyl-2-methylalanine (NBMA) is *ortho*-hydroxylated stereoselectively by trimethylamine *N*-oxide (TMAO).

References

- 1 (a) G. B. SHUL'PIN, *Organic Reactions Catalyzed by Metal Complexes*, Nauka, Moscow, 1988 (in Russian); (b) A. E. SHILOV, G. B. SHUL'PIN, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht Boston London, 2000, see for example: Chapter IX (Homogeneous catalytic oxidation of hydrocarbons by molecular oxygen), Chapter X (Homogeneous catalytic oxidation of hydrocarbons by peroxides and other oxygen atom donors), Chapter XI (Oxidation in living cells and its chemical models); (c) A. E. SHILOV, G. B. SHUL'PIN, *Chem. Rev.* 1997, 97, 2879–2932; (d) G. B. SHUL'PIN, *J. Mol. Catal. A: Chem.* 2002, 189, 39–66.
- 2 F. WIDDEL, R. RABUS, *Curr. Opin. Biotechnol.* 2001, 12, 259–276.
- 3 (a) J. HALPERN, *Pure Appl. Chem.* 2001, 73, 209–220; (b) C. JIA, D. PIAO, J. OYAMADA, W. LU, T. KITAMURA, Y. FUJIWARA, *Science* 2000, 287, 1992–1995; (c) C. JIA, T. KITAMURA, Y. FUJIWARA, *Acc. Chem. Res.* 2001, 34, 633–639; (d) V. V. GRUSHIN, W. J. MARSHALL, D. L. THORN, *Adv. Synth. Catal.* 2001, 343, 161–165; (e) T. ISHIYAMA, J. TAKAGI, J. F. HARTWIG, N. MIYaura, *Angew. Chem. Int. Ed.* 2002, 41, 3056–3058; (f) S. R. KLEI, J. T. GOLDEN, P. BURGER, R. G. BERGMAN, *J. Mol. Catal. A: Chem.* 2002, 189, 79–94; (g) K. KROGH-JESPERSEN, M. CZERW, A. S. GOLDMAN, *J. Mol. Catal. A: Chem.* 2002, 189, 95–110; (h) H. M. L. DAVIES, *J. Mol. Catal. A: Chem.* 2002, 189, 125–135.
- 4 (a) B. S. WILLIAMS, K. I. GOLDBERG, *J. Am. Chem. Soc.* 2001, 123, 2576–2587; (b) J. PROCELEWSKA, A. ZAHL, D. VAN ELDIK, H. A. ZHONG, J. A. LABINGER, J. E. BERCAW, *Inorg. Chem.* 2002, 41, 2808–2810; (c) V. V. ROSTOVTSSEV, L. M. HENLING, J. A. LABINGER, J. E. BERCAW, *Inorg. Chem.* 2002, 41, 3608–3619; (d) A. G. WONG-FOY, L. M. HENLING, M. DAY, J. A. LABINGER, J. E. BERCAW, *J. Mol. Catal. A: Chem.* 2002, 189, 3–16.
- 5 (a) B. D. DANGEL, J. A. JOHNSON, D. SAMES, *J. Am. Chem. Soc.* 2001, 123, 8149–8150; (b) N. DeVRIES, D. C. ROE, D. L. THORN, *J. Mol. Catal. A: Chem.* 2002, 189, 17–22; (c) R. A. PERIANA, D. J. TAUBE, S. GAMBLE, H. TAUBE, T. SATOH, H. FUJII, *Science* 1998, 280, 560–564; (d) W. V. KONZE, B. L. SCOTT, G. J. KUBAS, *J. Am. Chem. Soc.* 2002, 124, 12550–12556.
- 6 (a) E. I. SOLOMON, *Inorg. Chem.* 2001, 40, 3656–3669; (b) D. LEE, S. J. LIPPARD, *Inorg. Chem.* 2002, 41, 827–837; (c) V. P. BUI, T. HUDLICKY, T. V. HANSEN, Y. STENSTROM, *Tetrahedron Lett.* 2002, 43, 2839–2841; (d) X. RIBAS, D. A. JACKSON, B. DONNADIEU, J. MAHÍA, T. PARELLA, R. XIFRA, B. HEDMAN, K. O. HODGSON, A. LLOBET, T. D. P. STACK, *Angew. Chem. Int. Ed.* 2002, 41, 2991–2994; (e) G. B. MARAVIN, M. V. AVDEEV, E. I. BAGRIY, *Neftekhimiya* 2000, 40, 3–21 (in Russian); (f) J. T. GROVES, *J. Porphyrins Phthalocyanines* 2000, 4, 350–352; (g) A. P. NELSON, S. G. DIMAGNO, *J. Am. Chem. Soc.* 2000, 122, 8569–8570.
- 7 (a) M. BRÖNSTRUP, C. TRAGE, D. SCHRÖDER, H. SCHWARZ, *J. Am. Chem. Soc.* 2000, 122, 699–704; (b) M. BRÖNSTRUP, D. SCHRÖDER, H. SCHWARZ, *Chem. Eur. J.* 2000, 6, 91–103; (c) Y. SHIOTA, K. YOSHIZAWA, *J. Am. Chem. Soc.* 2000, 122, 1217–1232.
- 8 U. SCHUCHARDT, D. CARDOSO, R. SERCHELI, R. PEREIRA, R. S. DA CRUZ, M. C. GUERREIRO, D. MANDELLI, E. V. SPINACÉ, E. L. PIRES, *Appl. Catal. A: General* 2001, 211, 1–17.
- 9 (a) P. T. ANASTAS, J. C. WARNER, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998; (b) P. T. ANASTAS, M. M. KIRCHHOFF, T. C. WILLIAMSON, *Appl. Catal. A: General* 2001, 221, 3–13; (c) P. T. ANASTAS, M. M. KIRCHHOFF, *Acc. Chem. Res.* 2002, 35, 686–694.
- 10 (a) A. GOOSEN, C. W. MCCLELAND, D. H. MORGAN, J. S. O'CONNELL, A. RAMPLIN, *J. Chem. Soc. Perkin Trans. 2* 1993, 401–404; (b) YU. N. KOZLOV, G. B. SHUL'PIN, "Can methane and other alkanes be oxidized in solutions at low temperature via a classical radical-chain mechanism?", *The Chemistry Preprint Server*, <http://preprint.chemweb.com/physchem/0106002>, 2001, pp. 1–9.

- 11 (a) L. I. MATIENKO, L. A. MOSOLOVA, *Russ. Chem. Bull.* **1999**, *48*, 55–60; (b) Y. F. HSU, C. P. CHENG, *J. Mol. Catal. A: Chem.* **1998**, *136*, 1–11; (c) P. A. HAMLEY, T. ILKENHANS, J. M. WEBSTER, E. GARCIA-VERDUGO, E. VENARDOU, M. J. CLARKE, R. AUERBACH, W. B. THOMAS, K. WHISTON, M. POLIAKOFF, *Green Chem.* **2002**, *4*, 235–238; (d) A. M. KHENKIN, R. NEUMANN, *Inorg. Chem.* **2000**, *39*, 3455–3462; (e) A. I. NEKHAEV, R. S. BORISOV, V. G. ZAIKIN, E. I. BAGRII, *Petrol. Chem.* **2002**, *42*, 238–245; (f) T. V. MAKSIMOVA, T. V. SIROTA, E. V. KOVERZANOVA, A. M. KASHKAI, O. T. KASAIKINA, *Petrol. Chem.* **2002**, *42*, 46–50; (g) P. J. BARICELLI, V. J. SÁNCHEZ, A. J. PARDEY, S. A. MOYA, *J. Mol. Catal. A: Chem.* **2000**, *164*, 77–84; (h) D. A. M. BOGHAEL, S. MOHEBI, *J. Mol. Catal. A: Chem.* **2002**, *179*, 41–51; (i) D. M. BOGHAEL, S. MOHEBI, *Tetrahedron* **2002**, *58*, 5357–5366; (j) L. J. CSÁNYI, K. JÁKY, G. GALBÁCS, *J. Mol. Catal. A: Chem.* **2002**, *179*, 65–72; (k) A. K. EL-QISIARI, H. A. QASEER, P. M. HENRY, *Tetrahedron Lett.* **2002**, *43*, 4229–4231; (l) T. STRAUB, A. M. P. KOSKINEN, *Inorg. Chem. Commun.* **2002**, *5*, 1052–1055; (m) F. D'ACUNZO, P. BAIOTTO, M. FABBRINI, C. GALLI, P. GENTILI, *Eur. J. Org. Chem.* **2002**, 4195–4201; (n) M. K. LAJUNEN, T. MAUNULA, A. M. P. KOSKINEN, *Tetrahedron* **2000**, *56*, 8167–8171.
- 12 (a) P. D. METELSKI, V. A. ADAMIAN, J. H. ESPENSON, *Inorg. Chem.* **2000**, *39*, 2434–2439; (b) J. E. LYONS, P. E. ELLIS, JR., S. N. SHAIKH, *Inorg. Chim. Acta* **1998**, *270*, 162–168; (c) K. T. MOORE, I. T. HORVÁTH, M. J. THERIEN, *Inorg. Chem.* **2000**, *39*, 3125–3139; (d) J. HABER, L. MATACHOWSKI, K. PAMIN, J. POLTOWICZ, *J. Mol. Catal. A: Chem.* **2000**, *162*, 105–109; (e) for the Ishii oxidation reaction, see a book [1 b], a review: Y. ISHII, S. SAKAGUCHI, T. IWAHAMA, *Adv. Synth. Catal.* **2001**, *343*, 393–427; and recent articles: Y. TASHIRO, T. IWAHAMA, S. SAKAGUCHI, Y. ISHII, *Adv. Synth. Catal.* **2001**, *343*, 220–225; O. FUKUDA, S. SAKAGUCHI, Y. ISHII, *Adv. Synth. Catal.* **2001**, *343*, 809–813; A. SHIBAMOTO, S. SAKAGUCHI, Y. ISHII, *Tetrahedron Lett.* **2002**, *43*, 8859–8861; (f) S. SAKAGUCHI, T. HIRABAYASHI, Y. ISHII, *Chem. Commun.* **2002**, 516–517; (g) L. C. PASSONI, F. J. LUNA, M. WALLAU, R. BUFON, U. SCHUCHARDT, *J. Mol. Catal. A: Chem.* **1998**, *134*, 229–235; (h) O. FUKUDA, S. SAKAGUCHI, Y. ISHII, *Tetrahedron Lett.* **2001**, *42*, 3479–3481; (i) I. W. C. E. ARENDS, M. SASIDHARAN, A. KÜHNLE, M. DUDA, C. JOST, R. A. SHELDON, *Tetrahedron* **2002**, *58*, 9055–9061; (j) J.-M. BRÉGEAULT, F. LAUNAY, A. ATLAMSANI, *C. R. Acad. Sci Paris, Ser. IIc, Chemistry* **2001**, *4*, 11–26; (k) M. VENNAT, P. HERSON, J.-M. BRÉGEAULT, G. B. SHUL'PIN, *Eur. J. Inorg. Chem.* **2003**, 908–917; (l) L. EL AAKEL, F. LAUNAY, A. ATLAMSANI, J.-M. BRÉGEAULT, *Chem. Commun.* **2001**, 2218–2219; (m) R. YAMAHARA, S. OGO, H. MASUDA, Y. WATANABE, *J. Inorg. Biochem.* **2002**, *88*, 284–294.
- 13 (a) D. H. R. BARTON, T. LI, J. MACKINNON, *Chem. Commun.* **1997**, 557–558; (b) N. KOMIYA, T. NAOYA, Y. ODA, S.-I. MURAHASHI, *J. Mol. Catal. A: Chem.* **1997**, *117*, 21–37; (c) M. M. DELL'ANNA, P. MASTRORILLI, C. F. NOBILE, *J. Mol. Catal. A: Chem.* **1998**, *130*, 65–71; (d) K. MIKI, T. FURUYA, *Chem. Commun.* **1998**, 97–98; (e) I. YAMANAKA, K. MORIMOTO, M. SOMA, K. OTSUKA, *J. Mol. Catal. A: Chem.* **1998**, *133*, 251–254; (f) H. RÜDLER, B. DENISE, *J. Mol. Catal. A: Chem.* **2000**, *154*, 277–279; (g) J.-W. HUANG, W.-Z. HUANG, W.-J. MEI, J. LIU, S.-G. HU, L.-N. JI, *J. Mol. Catal. A: Chem.* **2000**, *156*, 275–278; (h) R. ÇELENLİGİL-ÇETİN, R. J. STAPLES, P. STAVROPOULOS, *Inorg. Chem.* **2000**, *39*, 5838–5846; (i) E. D. PARK, Y.-S. HWANG, J. S. LEE, *Catal. Commun.* **2001**, *2*, 187–190; (j) G. B. SHUL'PIN, A. E. SHILOV, G. SÜSS-FINK, *Tetrahedron Lett.* **2001**, *42*, 7253–7256; (k) N. THEYSSSEN, W. LEITNER, *Chem. Commun.* **2002**, 410–411; (l) J. E. REMIAS, A. SEN, *J. Mol. Catal. A: Chem.* **2002**, *189*, 33–38; (m) T. MIYAKE, M. HAMADA, H. NIWA, M. NISHIZUKA, M. OGURI, *J. Mol. Catal. A: Chem.* **2002**, *178*, 199–204; (n) G. B. SHUL'PIN, E. R. LACHTER "Aerobic hydroxylation of hydrocarbons catalysed by vanadate ion", *The Chemistry Preprint Server*, <http://preprint.chemweb.com/biochem/0204001>, **2002**, pp. 1–5; *J. Mol. Catal. A: Chem.* **2003**, *197*, 65–71; (o) C. BOLM, G. SCHLINGLOFF, F. BIENEWALD, *J. Mol. Cat-*

- al. A: *Chem.* **1997**, *117*, 347–350; (p) E. T. FARINAS, U. SCHWANEBERG, A. GLIEDER, F. H. ARNOLD, *Adv. Synth. Catal.* **2001**, *343*, 601–606.
- 14 (a) *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Ed.: G. STRUKUL), Kluwer Academic Publishers, Dordrecht, **1992**; C. W. JONES, *Applications of Hydrogen Peroxide and Derivatives*, The Royal Society of Chemistry, Cambridge, **1999**; T. J. COLLINS, *Acc. Chem. Res.* **2002**, *35*, 782–790; (b) G. B. SHUL'PIN, "Alkane oxidation: estimation of alkyl hydroperoxide content by GC analysis of the reaction solution samples before and after reduction with triphenylphosphine", *The Chemistry Preprint Server*, <http://preprint.chemweb.com/orgchem/0106001>, **2001**, pp. 1–6.
- 15 (a) G. B. SHUL'PIN, G. SÜSS-FINK, L. S. SHUL'PINA, *J. Mol. Catal. A: Chem.* **2001**, *170*, 17–34; (b) G. B. SHUL'PIN, G. V. NIZOVA, YU. N. KOZLOV, I. G. PECHENKINA, *New J. Chem.* **2002**, *26*, 1238–1245; (c) G. V. NIZOVA, C. BOLM, S. CECCARELLI, C. PAVAN, G. B. SHUL'PIN, *Adv. Synth. Catal.* **2002**, *344*, 899–905; (d) T. H. BENNUR, S. SABNE, S. S. DESHPANDE, D. SRINIVAS, S. SIVASANKER, *J. Mol. Catal. A: Chem.* **2002**, *185*, 71–80.
- 16 (a) YU. N. KOZLOV, G. V. NIZOVA, G. B. SHUL'PIN, *Russ. J. Phys. Chem.* **2001**, *75*, 770–774; (b) G. B. SHUL'PIN, YU. N. KOZLOV, G. V. NIZOVA, G. SÜSS-FINK, S. STANISLAS, A. KITAYGORODSKIY, V. S. KULIKOVA, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1351–1371; (c) M. H. C. DE LA CRUZ, YU. N. KOZLOV, E. R. LACHTER, G. B. SHUL'PIN, "Kinetics and mechanism of the benzene hydroxylation by the 'O₂-H₂O₂-vanadium derivative-pyrazine-2-carboxylic acid' reagent", *The Chemistry Preprint Server*, <http://preprint.chemweb.com/orgchem/0205002>, **2002**, pp. 1–9; *New J. Chem.* **2003**, *27*, 634–638.
- 17 (a) A. KOZLOV, K. ASAKURA, Y. IWASAWA, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 809–816; (b) A. KOZLOV, A. KOZLOVA, K. ASAKURA, Y. IWASAWA, *J. Mol. Catal. A: Chem.* **1999**, *137*, 223–237; (c) P. M. REIS, J. A. L. SILVA, J. J. R. FRAÛSTO DA SILVA, A. J. L. POMBEIRO, *Chem. Commun.* **2000**, 1845–1856; (d) G. SÜSS-FINK, L. GONZALEZ, G. B. SHUL'PIN, *Appl. Catal., A: General* **2001**, *217*, 111–117; (e) Y. SEKI, N. MIZUNO, M. MISONO, *Appl. Catal. A: General* **2000**, *194/195*, 13–20; (f) Y. SEKI, J. S. MIN, M. MISONO, N. MIZUNO, *J. Phys. Chem. B* **2000**, *104*, 5940–5944; (g) S. LIN, Y. ZHEN, S.-M. WANG, Y.-M. DAI, *J. Mol. Catal. A: Chem.* **2000**, *156*, 113–120.
- 18 (a) G. ROELFES, M. LUBBEN, R. HAGE, L. QUE, JR., B. L. FERGINGA, *Chem. Eur. J.* **2000**, *6*, 2152–2159; (b) K. CHEN, M. COSTAS, L. QUE, JR., *J. Chem. Soc., Dalton Trans.* **2002**, 672–679; (c) M. COSTAS, L. QUE, JR., *Angew. Chem. Int. Ed.* **2002**, *41*, 2179–2181; (d) Y. MEKMOUCHE, C. DUBOC-TOIA, S. MÉNAGE, C. LAMBEAUX, M. FONTECAVE, *J. Mol. Catal. A: Chem.* **2000**, *156*, 85–89; (e) G. V. NIZOVA, B. KREBS, G. SÜSS-FINK, S. SCHINDLER, L. WESTERHEIDE, L. GONZALEZ CUERVO, G. B. SHUL'PIN, *Tetrahedron* **2002**, *58*, 9231–9237; (f) G. B. SHUL'PIN, C. V. NIZOVA, YU. N. KOZLOV, L. GONZALEZ-CUERVO, G. SÜSS-FINK, *Adv. Synth. Catal.* **2004**, *346*, 317–332; (g) S. NISHINO, H. HOSOMI, S. OHBA, H. MATSUSHIMA, T. TOKII, Y. NISHIDA, *J. Chem. Soc., Dalton Trans.* **1999**, 1509–1513; (h) K. CHEN, L. QUE, JR., *J. Am. Chem. Soc.* **2001**, *123*, 6327–6337.
- 19 (a) E. BACIOCCHI, T. BOSCHI, L. CASSIOLI, C. GALLI, A. LAPI, P. TAGLIATESTA, *Tetrahedron Lett.* **1997**, *38*, 7283–7286; (b) A. M. D'A. ROCHA GONSALVES, A. C. SERRA, *J. Porphyrins Phthalocyanines* **2000**, *4*, 599–604; (c) J.-F. BARTOLI, K. LE BARCH, M. PALACIO, P. BATTIONI, D. MANSUY, *Chem. Commun.* **2001**, 1718–1719.
- 20 (a) R. BANDYOPADHYAY, S. BISWAS, S. GUHA, A. K. MUKHERJEE, R. BHATTACHARYA, *Chem. Commun.* **1999**, 1627–1628; (b) P. STAVROPOULOS, R. ÇELENİGİL-ÇETİN, A. E. TAPPER, *Acc. Chem. Res.* **2001**, *34*, 745–752; U. SCHUCHARDT, M. J. D. M. JANNINI, D. T. RICHENS, M. C. GUERREIRO, E. V. SPINACÉ, *Tetrahedron* **2001**, *57*, 2685–2688; (c) G. B. SHUL'PIN, G. SÜSS-FINK, L. S. SHUL'PINA, *J. Chem. Res. (S)* **2000**, 576–577; (d) G. B. SHUL'PIN, G. SÜSS-FINK, L. S. SHUL'PINA, *Chem. Commun.*, **2000**, 1131–1132; G. B. SHUL'PIN, G. SÜSS-FINK, *Petrol. Chem.* **2002**, *42*, 233–237; (e) G. B. SHUL'PIN, *J. Chem. Res. (S)*

- 2002, 351–353; (f) R. RUSS, T. ZELINSKI, T. ANKE, *Tetrahedron Lett.* **2002**, *43*, 791–793; (g) H. B. DUNFORD, *Coord. Chem. Rev.* **2002**, *233/234*, 311–318.
- 21 (a) J. JACOB, J. H. ESPENSON, *Inorg. Chim. Acta* **1998**, *270*, 55–59; (b) J.-F. BARTOLI, V. MOURIES-MANSUY, K. LE BARCH-OZETTE, M. PALACIO, P. BAITTONI, D. MANSUY, *Chem. Commun.* **2000**, 827–828; (c) N. A. ALEKAR, V. INDIRA, S. B. HALLIGUDI, D. SRINAVAS, S. GOPINATHAN, C. GOPINATHAN, *J. Mol. Catal. A: Chem.* **2000**, *164*, 181–189; (d) D. BIANCHI, R. BORTOLO, R. TASSINARI, M. RICCI, R. VIGNOLA, *Angew. Chem. Int. Ed.* **2000**, *39*, 4321–4323; (e) G. L. ELIZAROVA, L. G. MATVIENKO, A. O. KUZMIN, E. R. SAVINOVA, V. N. PARMON, *Mendeleev Commun.* **2001**, *11*, 15–17.
- 22 (a) W. A. HERRMANN, J. J. HAIDER, R. W. FISCHER, *J. Mol. Catal. A: Chem.* **1999**, *138*, 115–121; (b) O. A. ANUNZIATA, L. B. PIERELLA, A. R. BELTRAMONE, *J. Mol. Catal. A: Chem.* **1999**, *149*, 255–261; (c) S. NARAYANAN, K. V. V. S. B. S. R. MURTHY, K. M. REDDY, N. PREMCHANDER, *Appl. Catal. A: General* **2002**, *228*, 161–165.
- 23 (a) S.-I. MURAHASHI, N. KOMIYA, Y. HAYASHI, T. KUMANO, *Pure Appl. Chem.* **2001**, *73*, 311–314; (b) T. SOOKNOI, J. LIMTRAKUL, *Appl. Catal. A: General* **2002**, *233*, 227–237; (c) S. BANFI, M. CAVAZZINI, G. POZZI, S. V. BARKANOVA, O. K. KALIYA, *J. Chem. Soc., Perkin Trans 2* **2000**, 871–877; S. V. BARKANOVA, E. A. MAKAROVA, *J. Mol. Catal. A: Chem.* **2001**, *174*, 89–105; S. V. BARKANOVA, O. K. KALIYA, E. A. LUK'YANETS, *Mendeleev Commun.* **2001**, *11*, 116–118.
- 24 (a) G. B. SHU'PIN, J. GRADINARU, YU. N. KOZLOV, *Org. Biomol. Chem.* **2003**, *1*, 3611–3617; (b) L. GONZALEZ CUERVO, YU. N. KOZLOV, G. SÜSS-FINK, G. B. SHU'PIN, *J. Mol. Catal. A: Chem.* **2004**, in press; (c) G. SCHLINGLOFF, C. BOLM, in *Transition Metals for Organic Synthesis* (Eds.: M. BELLER, C. BOLM), Wiley-VCH, **1998**, *2*, 193–199. (d) J. LE BRAS, J. MÜZART, *J. Mol. Catal. A: Chem.* **2002**, *185*, 113–117; (e) G. CHELUCCI, G. LORIGA, G. MURINEDDU, G. A. PINNA, *Tetrahedron Lett.* **2002**, *43*, 3601–3604; (f) G. CHELUCCI, A. IULIANO, D. MURONI, A. SABA, *J. Mol. Catal. A: Chem.* **2003**, *191*, 29–33.
- 25 (a) T. KONOIKE, Y. ARAKI, Y. KANDA, *Tetrahedron Lett.* **1999**, *40*, 6971–6974; (b) H. R. KHAVASI, S. S. H. DAVARANI, N. SAFARI, *J. Mol. Catal. A: Chem.* **2002**, *188*, 115–122; (c) W. NAM, J. Y. RYU, I. KIM, C. KIM, *Tetrahedron Lett.* **2002**, *43*, 5487–5490; (d) C. J. MOODY, J. L. O'CONNELL, *Chem. Commun.* **2000**, 1311–1312; (e) N. KOMIYA, S. NOJI, S.-I. MURAHASHI, *Chem. Commun.* **2001**, 65–66; (f) J. R. LINDSAY SMITH, G. B. SHU'PIN, *Tetrahedron Lett.* **1998**, *39*, 4909–4912; G. B. SHU'PIN, J. R. LINDSAY SMITH, *Russ. Chem. Bull.* **1998**, *47*, 2379–2386.
- 26 (a) G. ROTHENBERG, L. FELDBERG, H. WIENER, Y. SASSON, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2429–2434; (b) U. SCHUCHARDT, R. PEREIRA, M. RUFO, *J. Mol. Catal. A: Chem.* **1998**, *135*, 257–262; (c) C. R. JACOB, S. P. VARKEY, P. RATNASAMY, *Appl. Catal. A: General* **1999**, *182*, 91–96; (d) K. NEIMANN, R. NEUMANN, A. RABION, R. M. BUCHANAN, R. H. FISH, *Inorg. Chem.* **1999**, *38*, 3575–3580; (e) J.-M. VINCENT, S. BÉARNAIS-BARBRY, C. PIERRE, J.-B. VERLHAC, *J. Chem. Soc., Dalton Trans.* **1999**, 1913–1914; (f) M. ROGOVINA, R. NEUMANN, *J. Mol. Catal. A: Chem.* **1999**, *138*, 315–318; (g) M. COSTAS, A. LLOBET, *J. Mol. Catal. A: Chem.* **1999**, *142*, 113–124; (h) C.-M. CHE, K.-W. CHENG, M. C. W. CHAN, T.-C. LAU, C.-K. MAK, *J. Org. Chem.* **2000**, *65*, 7996–8000; (i) A. A. VALENTE, J. VITAL, *J. Mol. Catal. A: Chem.* **2000**, *156*, 163–172; (j) D. CHATTERJEE, A. MITRA, *Inorg. Chem. Commun.* **2000**, *3*, 640–644; (k) J. A. R. SALVADOR, J. H. CLARK, *Chem. Commun.* **2001**, 33–34; (l) G. BLAY, I. FERNÁNDEZ, T. GIMÉNEZ, J. R. PEDRO, R. RUIZ, E. PARDO, F. LLORET, M. C. MUOZ, *Chem. Commun.* **2001**, 2102–2103; (m) D. CHATTERJEE, A. MITRA, S. MUKHERJEE, *J. Mol. Catal. A: Chem.* **2001**, *165*, 295–298; (n) G. B. SHU'PIN, *Petrol. Chem.* **2001**, *41*, 405–412; (o) J. ZAWADIAK, D. GILNER, R. MAZURKIEWICZ, B. ORLINSKA, *Appl. Catal. A: General* **2001**, *205*, 239–243; (p) J.-F. PAN, K. CHEN, *J. Mol. Catal. A: Chem.* **2001**, *176*, 19–22; (q) J. A. R. SALVADOR, J. H. CLARK, *Green*

- Chem.* **2002**, *4*, 352–356; (r) T. G. CARRELL, S. COHEN, G. C. DISMUKES, *J. Mol. Catal. A: Chem.* **2002**, *187*, 3–15; (s) N. GROOTBOOM, T. NYOKONG, *J. Mol. Catal. A: Chem.* **2002**, *179*, 113–123; (t) M. NOWOTNY, L. N. PEDERSEN, U. HANEFELD, T. MASCHMEYER, *Chem. Eur. J.* **2002**, *8*, 3724–3731; (u) G. B. SHUL'PIN, J. GRADINARU, YU. N. KOZLOV, *Org. Biomol. Chem.* **2003**, *1*, 2303–2306; (v) B. MEUNIER, *Chem. Rev.* **1992**, *92*, 1411–1456.
- 27** (a) M. V. AVDEEV, E. I. BAGRII, G. B. MARAVIN, YU. M. KOROLEV, R. S. BORISOV, *Petrol. Chem.* **2000**, *40*, 391–398; (b) A. CAGNINA, S. CAMPESTRINI, F. DI FURIA, P. GHIOTTI, *J. Mol. Catal. A: Chem.* **1998**, *130*, 221–231; (c) L. CAMMAROTA, S. CAMPESTRINI, M. CARRIERI, F. DI FURIA, P. GHIOTTI, *J. Mol. Catal. A: Chem.* **1999**, *137*, 155–160; (d) N. D'ALESSANDRO, L. LIBERATORE, L. TONUCCI, A. MORVILLO, M. BRESSAN, *New J. Chem.* **2001**, *25*, 1319–1324; (e) D. MOHAJER, A. REZAEIFARD, *Tetrahedron Lett.* **2002**, *43*, 1881–1884.
- 28** (a) Y. FUJIWARA, C. JIA, *Pure Appl. Chem.* **2001**, *73*, 319–324; (b) W. LU, Y. YAMAO-KA, Y. TANIGUCHI, T. KITAMURA, K. TAKAKI, Y. FUJIWARA, *J. Organomet. Chem.* **1999**, *580*, 290–294; (c) P. M. REIS, J. A. L. SILVA, A. F. PALAVRA, J. J. R. FRAÚSTO DA SILVA, T. KITAMURA, Y. FUJIWARA, A. J. L. POMBEIRO, *Angew. Chem. Int. Ed.* **2003**, *42*, 821–823.
- 29** (a) Z. GROSS, L. SIMKOVICH, *Tetrahedron Lett.* **1998**, *39*, 8171–8174; (b) X.-B. ZHANG, C.-C. GUO, J.-B. XU, R.-Q. YU, *J. Mol. Catal. A: Chem.* **2000**, *154*, 31–38; (c) F. G. DORO, J. R. LINDSAY SMITH, A. G. FERREIRA, M. D. ASSIS, *J. Mol. Catal. A: Chem.* **2000**, *164*, 97–108; (d) J. DUXIAO, S. LINGYING, Z. SHENJIE, G. MINGDE, *J. Chem. Res. (S)* **2001**, 24–25; (e) F. S. VINHADO, C. M. C. PRADO-MAN-*SO*, H. C. SACCO, Y. IMAMOTO, *J. Mol. Catal. A: Chem.* **2001**, *174*, 279–288; (f) C.-C. GUO, X.-Q. LIU, Z.-P. LI, D.-C. GUO, *Appl. Catal. A: General* **2002**, *230*, 53–60.
- 30** (a) K. JITSUKAWA, Y. OKA, H. EINAGA, H. MASUDA, *Tetrahedron Lett.* **2001**, *42*, 3467–3469; (b) T. HAMADA, R. IRIE, J. MIHARA, K. HAMACHI, T. KATSUKI, *Tetrahedron* **1998**, *54*, 10017–10028; (c) R. F. MOREIRA, P. M. WHEN, D. SAMES, *Angew. Chem. Int. Ed.* **2000**, *39*, 1618–1621; (d) J. YANG, R. BRESLOW, *Angew. Chem. Int. Ed.* **2000**, *39*, 2692–2694; R. BRESLOW, J. YAN, S. BELVEDERE, *Tetrahedron Lett.* **2002**, *43*, 363–365; R. BRESLOW, Z. FANG, *Tetrahedron Lett.* **2002**, *43*, 5197–5200; (e) R. BRESLOW, J. YANG, J. YAN, *Tetrahedron* **2002**, *58*, 653–658; (f) P. M. WHEN, J. DU BOIS, *J. Am. Chem. Soc.* **2002**, *124*, 12950–12951.
- 31** (a) Y. SASSON, A. E.-A. A. QUNTAR, A. ZORAN, *Chem. Commun.* **1998**, 73–74; (b) V. S. KULIKOVA, M. M. LEVITSKY, A. F. SHESTAKOV, A. E. SHILOV, *Russ. Chem. Bull.* **1998**, *47*, 435–437; (c) T. YAMATO, N. SHINODA, T. KANAKOGI, *J. Chem. Res. (S)* **2000**, 522–523; (d) V. MIRKHANI, S. TANGESTANINEJAD, M. MOGHADAM, *J. Chem. Res. (S)* **1999**, 722–723; (e) S. YAMAZAKI, *Tetrahedron Lett.* **2001**, *42*, 3355–3357; (f) L. E. FIRDOUSI, A. BAQQA, S. ALLAOU, B. A. ALLAL, A. KARIM, Y. CASTANET, A. MORTREUX, *J. Mol. Catal. A: Chem.* **1998**, *135*, 11–22; (g) A. M. KHENKIN, R. NEUMANN, *J. Am. Chem. Soc.* **2002**, *124*, 4198–4199; (h) W. BUIJS, P. COMBA, D. CORNELI, H. PRITZKOW, *J. Organometal. Chem.* **2002**, *641*, 71–80.
- 32** (a) T. SHINGAKI, K. MIURA, T. HIGUCHI, M. HIROBE, T. NAGANO, *Chem. Commun.* **1997**, 861–862; (b) R. ZHANG, W.-Y. YU, T.-S. LAI, C.-C. CHE, *Chem. Commun.* **1999**, 1791–1792; (c) S. M. LEE, P. L. FUCHS, *J. Am. Chem. Soc.* **2002**, *124*, 13978–13979.