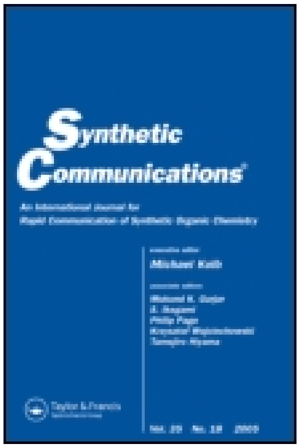
This article was downloaded by: [Fordham University]
On: 02 July 2013, At: 09:00
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SUPPORTED METALATED PHTHALOCYANINE AS CATALYST FOR OXIDATION BY MOLECULAR OXYGEN. SYNTHESIS OF QUINONES AND CARBONYL COMPOUNDS

Didier Villemin [a] , Mohamed Hammadi [b] & Messaoud Hachemi [b]

[a] Université de Caen, Ecole Nationale Supérieure d'Ingénieurs de Caen, ISMRA, CNRS UMR 6507, Caen, F-14050, France

[b] Université de Boumerdès, Faculté des Sciences, Boumerdes, 35000, Algérie

Published online: 12 Dec 2006.

To cite this article: Didier Villemin , Mohamed Hammadi & Messaoud Hachemi (2002) SUPPORTED METALATED PHTHALOCYANINE AS CATALYST FOR OXIDATION BY MOLECULAR OXYGEN. SYNTHESIS OF QUINONES AND CARBONYL COMPOUNDS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:10, 1501-1515, DOI: 10.1081/SCC-120004139

To link to this article: http://dx.doi.org/10.1081/SCC-120004139

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS, 32(10), 1501–1515 (2002)

SUPPORTED METALATED PHTHALOCYANINE AS CATALYST FOR OXIDATION BY MOLECULAR OXYGEN. SYNTHESIS OF QUINONES AND CARBONYL COMPOUNDS

Didier Villemin,[1,]* Mohamed Hammadi,[1,2]
and Messaoud Hachemi[1,2]

[1]Ecole Nationale Supérieure d'Ingénieurs de Caen,
ISMRA, CNRS UMR 6507, Université de Caen,
F-14050, Caen, France
[2]Université de Boumerdès, Faculté des Sciences,
35000 Boumerdes, Algérie

ABSTRACT

Supported metalated phthalocyanine on K10 or on lamellar zirconium phosphate catalyses the oxidation of hydroquinones (and phenols) into quinones. Some interesting natural napthoquinones were also prepared (Juglone, Menadione, Lawsone, Phthiocol). Supported metalated phthalocyanine was also used in re-oxidation by oxygen of palladium and ruthenium, in the Wacker oxidation of olefins into ketones, in the oxidation of cyclohexadiene and in oxidation of benzylic alcohols in aldehydes.

---

*Corresponding author. E-mail: didier.villemin@ismra.fr

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

The oxidation of phenols into quinones is a reaction of synthetic interest. The phenol oxidation products are used for the synthesis of natural products such as vitamins and their intermediates. Concerning the oxidation of phenols or hydroquinones into quinones, numerous oxidants were described in the literature such as chromic oxide,[1] silver oxide,[2] and ceric ammonium nitrate.[3] However, only few reactions use air or oxygen as the oxidant. On economic and ecological grounds, there is an increasing need for the development of soft processes, without toxic salts and which do not necessitate high temperature or high pressure.[4] Our attention was focused on the synthesis of new types of solid catalysts and their applications in soft oxidation in fine chemistry.

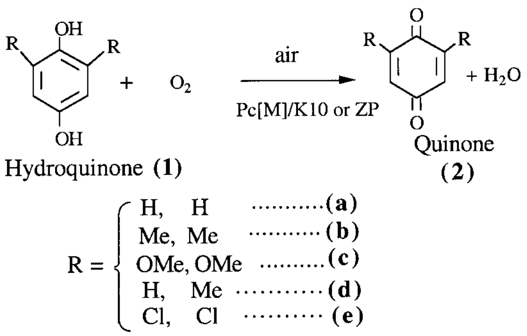
Phthalocyanines on different inorganic supports like silica,[5] alumina,[6] zeolite,[7] titanium oxide,[8] or coal,[9] were described as redox catalysts. We have shown[10] that the microwave irradiation at 2450 MHz of a mixture of metallic hydrated salt and phthalonitrile conducted quantitatively to the metalated phthalocyanine. The reaction of phthalonitrile with a montmorillonite K10 or a zirconium phosphate exchanged by metallic ions under microwave irradiation allows a fast preparation of metalated phthalocyanines supported on the layers of these inorganic solids. In the same way, it was also possible to use a zeolite (LSY-52 and 13X) in order to prepare metalated phthalocyanine encapsulated in the pores of the zeolites. The formed materials were identical to those obtained by classical conditions[11] but the pores of zeolite do not allow the use of such catalyst in fine chemistry.

It was shown that the phthalocyanines in solution catalysed the oxidation of the hydroquinone into quinone by oxygen.[12] Herein, we have been interested by the aerobic oxidation of phenols catalysed by supported metalated phthalocyanine on lamellar solids.

Oxidation of Hydroquinones (and Phenols) in Quinones

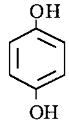
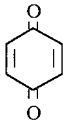
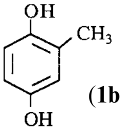
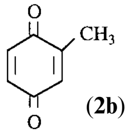
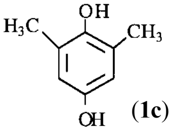
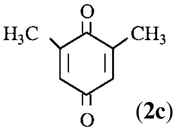
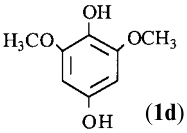
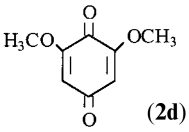
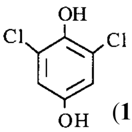
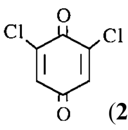
In a preliminary study, we have tested the oxidation of hydroquinone into quinone by air catalysed by a metalated phthalocyanine (Pc [M]) on the sheet of a montmorillonite K10 or zirconium phosphate (ZP). Hydroquinone was easily oxidised at room temperature in quinone by using PcFe/K10 and air (1 atm), as indicated in Scheme 1. The reaction can be generalised to substituted hydroquinones obtained from substituted phenols by an Elb reaction;[13] they were easily oxidised at room temperature in quinone by using PcFe/K10 and air (0.5 to 2 h).

Results obtained from different phenols were reported in Table 1.



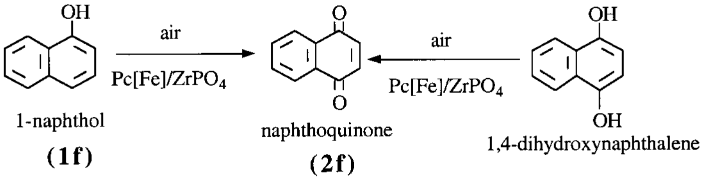
Scheme 1. Oxidation of hydroquinones.

Table 1. Oxidation of Hydroquinone into Quinone with Supported Metalated Phthalocyanines

Hydroquinones	Catalysts	Quinones	Yield (%)
 **(1a)**	Pc[Fe]/K10	 **(2a)**	98
 **(1b)**	Pc[Co]/K10	 **(2b)**	95
 **(1c)**	Pc[Co]/K10	 **(2c)**	90
 **(1d)**	Pc[Fe]/K10	 **(2d)**	89
 **(1e)**	Pc[Fe]/ZP	 **(2e)**	94

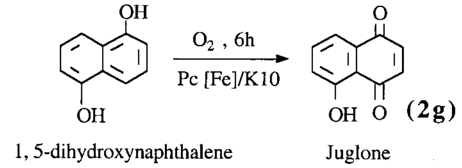
Whatever the nature of the support of metalated phthalocyanine [montmorillonite K10 or a zirconium phosphate ($ZrPO_4$)], and whatever the metal (Fe, Co, Mn) of the phthalocyanine tested, the reactions of oxidation of hydroquinones were quasi similar. The direct oxidation of phenols with oxygen in presence of supported metal phthalocyanines as oxidant generally gave quinone at room temperature, but the reaction is very slow and not selective.

We have also tested this type of reaction in naphthoquinone series. Many of naphthoquinones are natural products with interesting biological properties. The 1,4-dihydroxynaphthalene and the 1-naphthol have been transformed in naphthoquinone with the yield of 96% (1 h) and 65% (18 h), respectively, according to the Scheme 2.



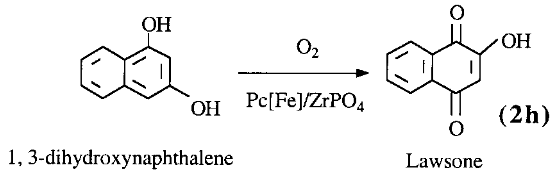
Scheme 2. Synthesis of naphthoquinone.

The catalytic system PcFe/K10, in presence of pure oxygen, oxidises easily the 1,5-dihydroxynaphthalene in 5-hydroxynaphthoquinone or Juglone[14] (79% yield). The latter is used as an alimentary stain for soft drinks. The total oxidation was about 6 h (Scheme 3) at room temperature.



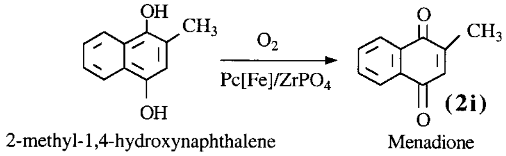
Scheme 3. Synthesis of Juglone.

The 1,3-dihydroxynaphtalene was oxidised in the same conditions in 2-hydroxynaphthoquinone (or Lawsone) (80% yield) as shown in Scheme 4. The latter is a natural colouring extracted from Henna (Lawsonia-lythraces) used like protective sun.[15]



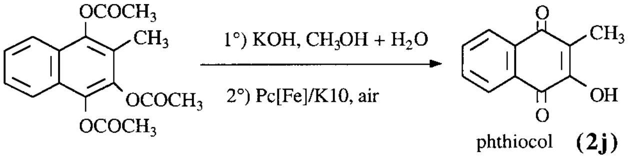
Scheme 4. Synthesis of Lawsone.

Menadione, which is the vitamin K3 carrier,[15] was obtained (yield 80% after 70 min) also by catalytic oxidation with Pe[Fe]/ZrPO$_4$ in the presense of pure oxygen from 2-methyl-1,4-dihydroxynaphthalene, according to Scheme 5.



Scheme 5. Synthesis of Menadione.

Menadione treated with acetic anhydride in the presence of triflic acid converts into the methyl triacetoxynaphtalene.[16] This ester is saponified by KOH, oxidised by the air in presence of K10/Pc Fe and has given the antibiotic Phthiocol[17] (75% yield after 20 min), according the Scheme 6.



Scheme 6. Synthesis of Phthiocol.

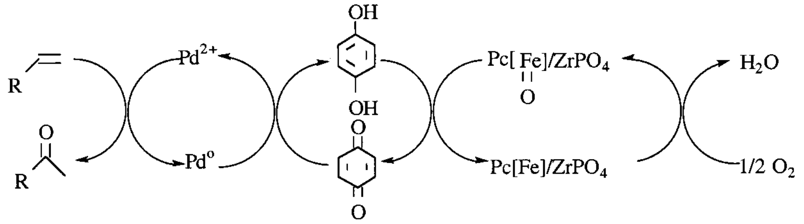
Reoxidation of Transition Metal Catalysts

We have shown that the phthalocyanines supported on the montmorillonite K10 or on zirconium phosphate catalysed the oxidation of the hydroquinone into quinone by the air at ambient temperature. The oxidation was quantitative whatever the nature of the support: montmorillonite, or zirconium phosphate, and whatever the metal (Fe, Co, Mn) of the phthalocyanine tested. Bäckvall[12,18] has used the quinone/hydroquinone system in solution for re-oxidation of the palladium and the ruthenium in selected three step reversible electron transfer processes under aerobic conditions. Therefore we have tested the system of heterogeneous hydroquinone/K10Pc[M] (M = Fe, Mn) in the presence of oxygen as a re-oxidant of palladium and ruthenium. This triple catalytic system was applied to three principal types of reactions:

(i) oxidation of terminal olefins to ketones (Wacker oxidation);
(ii) diacetoxylation of cyclic olefins;
(iii) oxidation of benzilic alcohols.

Oxidation of Terminal Alkenes

We have applied the method developed by Bäckvall et al.[18] to the oxidation in a solution of terminal alkenes to ketones for our heterogeneous catalyst. For this, we have used the ferrous phthalocyanine intercalated in zirconium phosphate as catalyst for the aerobic oxidation of hydroquinone to quinone. This one-pot triple catalytic system was indicated in the Wacker process described in Scheme 7.



Scheme 7. Catalytic cycle of Wacker oxidation.

There is an electron transfer from the substrate to Pd(II) giving Pd (0), followed by another electron transfer from Pd (0) to quinone. The hydroquinone thus formed transfers an electron to the oxidised form of the metal macrocycle, which is reduced. The latter is deoxidised by electron transfer by an oxygen molecule.

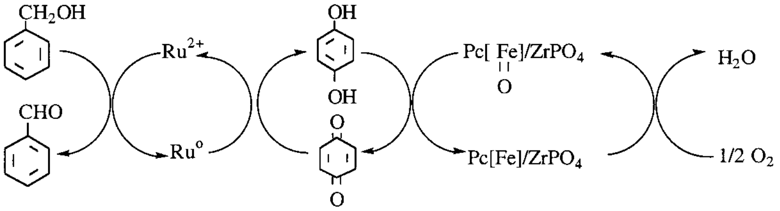
The results obtained with Pc[Fe]\ZrPO$_4$ were reported in Table 2.

Table 2. Oxidation of Olefin with $PdCl_2/Pc[Fe]\backslash ZrPO_4/O_2$

Alkenes	Catalyst	Ketones	Conversion/ Selectivity
Dodecene	$PdCl_2$	2-Dodecanone	82/78
1-Hexadecene	$PdCl_2$	2-Hexadecanone	82/75
Cyclododecene	$PdCl_2$	Cyclododecanone	85/83

Oxidation of Allylic and Benzylic Alcohols

In similar fashion, benzylic alcohol was oxidised into benzaldehyde using the ruthenium complex $RuCl_2(PPh_3)_3$[19] and the ferrous phthalocyanine intercalated in zirconium phosphate in presence of oxygen. The tripley catalysed reaction is illustrated by Scheme 8. The conversion was almost quantitative (90–98%).



Scheme 8. Catalytic cycles of oxidation of benzylic alcohol.

Diacetoxylation of 1,3-Cyclohexadiene

Allylic oxidation under homogeneous conditions was described by Bäckvall.[18] We have studied the allylic oxidation of 1,3-cyclohexadiene into 1,4-diacetoxy-2-cyclohexene under heterogeneous conditions with $Pc[Fe]/ZrPO_4$ as a catalyst for the re-oxidation of quinone. The 1,4-diacetoxy-2-cyclohexene was isolated (50% yield).

In all cases, the supported metalated phthalocyanine was active as a free metalated phthalocyanine. The exact role of the support was not studied. The supported metalated phthalocyanine could be recovered by centrifugation of the reactive mixture. The activity of supported metalated phthalocyanine was preserved.

EXPERIMENTAL

Proton NMR spectra (PMR) were determined on a Brucker AC 250 (250 MHz, $CDCl_3$, Me_4Si). Melting points (M.p.) in °C were uncorrected. Visible and ultraviolet spectra were performed on a Perkin-Elmer Lambda 15UV spectrometer. IR spectra were run with a 16PC FT-IR. Microwave irradiation was carried out with a commercial microwave oven (Toshiba ER 7620) at 2450 MHz and with resonance cavity TE_{O13} joined to a MES 73-800 generator of microwaves. Mass spectra were carried out on a Nermag Riber R10; TLC analyses were performed by using Kieselgel Schleicher and Schull F 1500 LS 254 and Merck 60 F 254. The grinding of the products were carried out on a analytical grinder A 10 of Janke and Kenkel-IKA Labortechnik.

The montmorillonite K10 was obtained from the firm of Süd Chemie and the zirconium phosphate from the firm BDH. The *tris*(triphenylphosphine) ruthenium (II) chloride [$RuCl_2(PPh_3)_3$] was prepared according to the literature.[19]

Preparation of Montmorillonite K10 Exchanged by M^{n+}

In a 250 ml flask, the montmorillonite K10 (8 g) was added to a solution of metallic salt (0.1 mol) [$(NH_4)_2Fe(SO_4)_2$, $CoCl_2$ or $Mn(OCOCH_3)_2$] dissolved in 100 ml of distilled water. The reactional mixture was stirred for 24 h at room temperature. The suspension was washed twice with distilled water then centrifuged. The montmorillonite exchanged by M^{n+} was washed with methanol and re-centrifuged. The solid was dried for 24 h in vacuum then finely ground. The final product was a clear beige colour.

Preparation of Zirconium Phosphate ($ZrPO_4$) Exchanged by M^{n+}

A 250 ml flask containing 5 g of zirconium phosphate dissolved in 25 ml of distilled water was added to a solution (0.1 mol) of metallic salt (100 ml). The mixture was stirred for 3 h then left standing for 2 h. After having decanted the solution, the operation was repeated four times with a successive change of the ferric solution. The solid was washed two times with distilled water (100 ml) then with methanol. After centrifugation, the solid was dried for 24 h in a vacuum.

Preparation of Zeolites Exchanged by M^{n+}

The zeolites LZY-52 and 13 X have been exchanged by Fe^{3+} according to the same experimental procedure to that of zirconium phosphate.

Phthalocyanines Intercalated in the K10 and in the Zirconium Phosphate

General procedure: A solution of phthalonitrile (10 mmol, 1.28 g) dissolved in 10 ml of dichloromethane was added to the solid ($ZrPO_4$ or K10; 2.5 g) exchanged with some metallic cations. After contact for 1.5 h, the remaining liquid was evaporated under reduced pressure. The activation of the solid under microwave irradiation (P = power, t = time of irradiation) was carried out in a resonance cavity. After cooling, the solid was successively washed with water, acetone (15 ml) and then with dichloromethane (15 ml). The solid was dried under reduced pressure and then extracted with acetonitrile as a solvent using a Soxhlet for 8 h. Catalysts were characterised by FT-IR, electronic spectra, Debye-Schere RX and elemental analysis. Electronic spectra of metalated phthalocyanine intercalated into montmorillonite or zirconium phosphate was very close to those observed with pure metalated phthalocyanine, but the bands were shifted.

Pc [Fe^{3+}] Supported on K 10: [$P = 540$ W, $t = 10$ min]. UV–Visible λ_{max} log(ε)/(1-chloronaphthalene): 6988 (3.37); 6626 (3.41); 5976 (3.22). IR (KBr) cm^{-1}: 3436, 1632, 1580, 1526, 1442, 1366, 1044, 798, 524.

Pc [Fe^{3+}] Supported on $ZrPO_4$: [$P = 540$ W, $t = 10$ min]. λ_{max} log(ε)/(1-chloronaphthalene): 6980 (3.45); 6632 (3.48); 6352 (3.18); 6023 (3.05). IR (KBr) cm^{-1}: 3446, 1648, 1564, 1526, 1444, 1400, 1056, 766, 516.

Pc[Co^{2+}] Supported on K10: [$P = 490$ W, $t = 10$ min]. UV–Visible λ_{max} log(ε)/(1-chloronaphthalene): 6695 (4.42); 6421 (3.88); 6042 (3.78); 5800 (3.22). IR (KBr) cm^{-1}: 1636, 1522, 1400, 1044, 796, 756, 732, 525, 466.

Pc[Co^{2+}] Supported on $ZrPO_4$: [$P = 480$ W, $t = 10$ min]. UV–Visible λ_{max} log (ε/(1-chloronaphthalene): 6712 (4.31); 6376 (3.91); 6072 (3.69); 5505 (2.95). IR (KBr) cm^{-1}: 1654, 1560, 1508, 1490, 1400, 1054, 800, 732, 528

Pc[Mn^{2+}] Supported on K10: [$P = 630$ W, $t = 10$ min]. UV–Visible λ_{max} log(ε)/(1-chloronaphthalene): 7287 (4.29); 6782 (3.97); 6491 (3.81); 5374 (3.35). IR (KBr) cm^{-1}: 1582, 1420, 1293, 1044, 967, 910, 870, 781, 738, 533.

Pc[Mn^{2+}] Supported on $ZrPO_4$: [$P = 630$ W, $t = 10$ min]. UV–Visible λ_{max} log (ε)/(1-chloronaphthalene): 6976 (4.37); 6635 (3.99); 6352 (3.41); 6035 (3.27). IR (KBr) cm^{-1}: 1581, 1418, 1297, 1044, 965, 908, 872, 779, 738, 534.

Pc[Co^{2+}] Supported on LZY-52: [$P = 630$ W, $t = 20$ min]. UV–Visible λ_{max} log (ε/(1-chloronaphthalene): 7807 (2.63); 7343 (2.85); 6697 (4.02); 6003

(3.68); 5810 (3.29). IR (KBr) cm^{-1}: 1698, 1684, 1636, 1576, 1570, 1522, 1490, 1472, 1404, 1009, 788, 720, 668, 580, 454.

Pc[Co^{2+}] Supported on 13 X: [$P = 630\,W$, $t = 20\,min$]. UV–Visible λ_{max} log(ε)/(1-chloronaphthalene): 6690 (4.39); 6001 (3.44); 5827 (3.08). IR (KBr) cm^{-1}: 1697, 1682, 1636, 1577, 1489, 1472, 1406, 1011, 722, 581, 454.

Pc[Fe^{2+}] Supported on LZY-52: Prepared by impregnation with a solution ferrocene in acetone [$P = 630\,W$, $t = 20\,min$]. UV-Visible λ_{max} log(ε)/(1-chloronaphthalene): 6975 (3.63); 6635 (3.87); 6330 (3.41); 5998 (3.34). IR (KBr) cm^{-1}: 3474, 1644, 1569, 1404, 1278, 1024, 790, 580.

Pe[Fe^{2+}] Supported on 13 X: Prepared by impregnation with a solution ferrocene in acetone [$P = 630\,W$, $t = 20\,min$]. UV-Visible λ_{max} log(ε)/(1-chloronaphthalene): 6981 (3.58); 6634 (3.91); 6331 (3.35); 6012 (3.26). IR (KBr) cm^{-1}: 3482, 1664, 1566, 1406, 1048, 978, 752, 672, 562.

Hydroquinones were prepared by the Elb reaction of phenols. In a typical experiment, the *m*-cresol (100 mmol; 10.81 g) was dissolved in 200 ml of 10% solution of sodium hydroxide under stirring at room temperature. A saturated aqueous solution of sodium persulfate (100 mmol; 23.8 g) was slowly and carefully added for 3 h. At the end of the addition, stirring was maintained at room temperature. The mixture stood overnight. The solution was acidified with Congo red and was extracted twice with ether. The aqueous layer was treated with an excess of hydrochloric acid and warmed in a steam bath for 30 min. After cooling, it was once again extracted with ether. The extracted organic layers were combined, dried on magnesium sulfate and finally distilled to afford the corresponding hydroquinone.

2-Methylhydroquinone (1b): Yield: 66%, brown solid, m.p. °C: 132–133, $C_7H_8O_2$, Calcd H 6.5% C 67.73%, Found H 6.61% C 67.62%. NMR ^{1}H ($CDCl_3$) δ 2.22 (s, 3H, CH_3); 6.45–6.72 (m, 3H, H arom); 7.18 (s, 1H, OH); 7.49 (s, 1H, OH): IR (KBr) cm^{-1}: 3374 (ν OH), 3038, 2978, 1652, 1591, 1490, 1464, 1442, 1282, 1244, 1156, 928, 856, 776.

2,6-Dimethoxylhydroquinone (1d): Prepared from 2,6-dimethoxyphenol (104 mmol; 16.21 g) and sodium persulfate (100 mmol; 23.8 g). Yield: 69%, brown solid, m.p. °C: 149, $C_8H_{10}O_4$, Calcd H 5.92% C 56.47%, Found H 5.85% C 56.38%. NMR ^{1}H ($CDCl_3$) δ: 3.81 (s, 6H, OCH_3); 7.64 (s, 1H, H arom); 7.91 (s, 1H, H arom). IR (KBr) cm^{-1}: 3420 (ν OH), 3062, 2952, 2852, 1696, 1646, 1594, 1482, 1322, 1260, 1220, 1108, 878, 668, 605.

Oxidation to Quinone

General procedure: In a typical experiment, a current of air was passed through a U tube fitted with a filter flask. The tube contains the supported phthalocyanine (0.1 g) in suspension in a solution of hydroquinone or phenol (5 mmol) dissolved in 10 ml of a mixture of dioxane/water (60 : 40) for 6 h at room temperature. The oxidation of phenol was followed by TLC. After the disappearance of phenol, the solution was filtered and evaporated under vacuum. The quinines were purified by chromatography on silica gel or by sublimation. All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. The UV spectra of quinones were carried out in a water–dioxane mixture.

1,4-Benzoquinone (2a): Yield: 98%, red solid, m.p. °C: 111, $C_6H_4O_2$, Calcd H 3.73% C 66.67%, Found Calcd H 3.65% C 66.57%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 244.4 (4.32), 302.4 (2.48), 433.6 (1.31), 4.53 (1.19). IR (KBr) cm^{-1}: 1684 (νC=O).

2-Methyl-1,4-benzoquinone (2b): Yield: 95%, brown solid, m.p. °C: 72–73, $C_7H_6O_2$, Calcd H 4.95% C 68.85%, Found H 4.87% C 68.73%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 278.2 (4.15), 312.3 (2.75), 422.6 (1.31) NMR ^1H ($CDCl_3$) δ: 2.01 (s, 1H, CH_3); 6.23 (s, 1H); 6.52 (m, 1H); 6.85 (d, 2H). IR (KBr) cm^{-1}: 1689 (νC=O).

2,6-Dimethylbenzoquinone (2c): Yield: 90%, brown solid, m.p. °C: 72, $C_8H_8O_2$, Calcd H 5.92% C 70.58%, Found H 6.01% C 70.50%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 270.6 (4.29), 318.1 (2.52), 414.3 (1.25). IR (KBr) cm^{-1}: 1685 (νC=O).

2,6-Dimethoxybenzoquinone (2d): Yield: 89%, brown solid, m.p. °C: 252–255, $C_8H_8O_2$, Calcd H 4.8% C 57.14%, Found H 4.87% C 57.12%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 279.5 (4.25), 3.79 (2.69), 465.5 (0.45). IR (KBr) cm^{-1}: 1678 (νC=O).

2,6-Dichlorobenzoquinone (2e): Yield: 94%, brown solid, m.p. °C: 118–120, $C_6H_2O_2Cl_2$, Calcd H 1.14% C 40.72%, Found H 1.25% C 40.43%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 277.4 (4.38), 3.25 (2.74) 432.6 (1.05). IR (KBr) cm^{-1}: 1683 (νC=O), 775 (νC-Cl).

Naphthoquinone (2f): Product formed by oxidation of 1-naphthol (0.74 g) and from 1,4-dihydroxynaphthalene (0.82 g) both in the presence of PcFe/$ZrPO_4$. Yield: 96%, m.p. °C: 119–120. $C_{10}H_6O_2$, Calcd H 3.82% C 75.94%, Found H 3.78% C 76.0%. UV–Visible λ_{max} log(ε) (dioxane/H_2O)/nm: 205.7 (1.23), 256.9 (4.22), 335.3 (3.39). NMR ^1H ($CDCl_3$) δ: 6.89 (s, 2H, CH=); 7.42–8.23 (m, 4H, H arom.). IR (KBr) cm^{-1}: 1673 (νC=O).

5-Hydroxy-1,4-naphthoquinone (Juglone) (2g): Product formed from 1,5-dihydroxynaphthalene in acetone. Yield: 87%, red brick solid, $C_{10}H_6O_3$, Calcd H 3.47% C 68.97%, Found H 3.58% C 68.90%. m.p. °C: 162. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 249.3 (4.21), 331.1 (3.18), 422.1 (2.98). NMR ^1H ($CDCl_3$) δ: 6.76 (s, 2H, CH=); 7.25–7.45

(m, 3H, H arom.). 7.77 (s, 1H, OH). IR (KBr) cm^{-1}: 3241 (νOH), 1683 (νC=O), 1587, 1170, 884, 535.

2-Hydroxy-1,4-naphthoquinone (Lawsone (2h): Yield 80%, orange solid. $C_{10}H_6O_3$, Calcd H 3.47% C 68.97%, Found H 3.53% C 68.92%. m.p. °C: 192. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 276.3 (4.48), 334.3 (3.28). NMR ^1H ($CDCl_3$) δ: 6.37 (s, 1H, OH); 7.26 (s, 1H, H arom.); 7.25–8.14 (m, 4H, H arom.). IR (KBr) cm^{-1}: 3166 (νOH), 1676 (νC=O), 1592, 1170, 874, 668, 536.

2-Methyl-1,4-naphthoquinone menadione (2i): Yield: 80%, yellow solid, m.p. °C: 105–106. $C_{11}H_8O_2$, Calcd H 4.38% C 78.25%, Found H 4.42% C 78.18%. UV–Visible λ_{max} log(ε) (dioxane/H_2O, 70 : 30)/nm: 264.1 (4.18), 332.5 (3.36). NMR ^1H ($CDCl_3$) δ: 2.21 (s. 3H, CH_3); 6.85 (s, 1H); 7.75–8.14 (m, 4H, H arom.). IR (KBr) cm^{-1}: 1732, 1668 (νC=O), 1593, 1082, 940, 884, 720, 650.

2-Hydroxy-3-methyl-1,4-naphthoquinone (phthiocol) (2j): Obtained from 2-methyl-1,3,4-triacetoxynaphthalene prepared from menadione.[16] The 1,2,4-triacetoxy-3-methylnaphthalene (632 mg, 2 mmol), dissolved in methanol (20 ml) was saponified by addition of sodium methoxide (324 mg, 6 mmol) and Pc[Fe]/$ZrPO_4$ (0.1 g) was added. An air-stream was passed in suspension for 1 h. After filtration and evaporation of methanol, the phthiocol was crystallised (357 mg, 95%). Yellow needles (cyclohexane), m.p. °C: 173–174 (ether + hexane). $C_{11}H_8O_3$, Calcd H 4.29% C 70.21%, Found H 4.35% C 70.08%. IR (KBr) cm^{-1}: 3330 (νOH), 1655 (νC=O). NMR ^1H ($CDCl_3$) δ: 2.08 (s, 3H, CH_3); 7.29 (s, 1H, OH); 7.5–8.1 (m, 4H, H arom.).

Oxidation of Alkenes to Ketones

General procedure: In a typical experiment, a mixture comprised of the alkene (5 mmol), palladium chloride (0.2 mmol; 0.35 mg), hydroquinone (1 mmol; 110 mg) and Pc[Fe]/$ZrPO_4$ (1 g) in aqueous DMF (DMF 2 ml, H_2O 0.2 ml) was introduced into a U tube. Oxygen (1 atm.; 50 ml min^{-1}) was bubbled through the solution for 3 h at room temperature. The mixture was centrifuged and methylene chloride (10 ml) was added to the supernatant. The organic solution was washed with a solution of 3N (10 ml) and then dried out on magnesium sulfate. The solvent was eliminated under reduced pressure. Products were identified by comparison of their retention times (gas chromatography) with authentic samples and purified by flash chromatography on silica.

2-Dodecanone: Obtained from 1-dodecene (1.10 ml), isolated yield 53%, $C_{12}H_{24}O$, Calcd H 13.12% C 78.2%, Found H 13.08% C 78.31%.

NMR ^{1}H ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.25 (m broad, 18H, CH_2), 1.95 (s, 3H, $COCH_3$), 2.2 (t, 2H, CH_2).

2-Hexadecanone: Obtained from 1-hexadecene (1.30 ml), isolated yield 49%, m.p. °C: 45. $C_{16}H_{32}O$, Calcd H 13.42% C 79.93%, Found H 13.40% C 80.06%. NMR ^{1}H ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1–1.5 (m, 30H, CH_2), 2 (s, 3H, $COCH_3$) 2.3 (t, 2H, CH_2).

Cyclododecanone: Obtained from cyclododecene (2.5 g), isolated yield 51%, m.p. °C: 60. $C_{12}H_{22}O$. Calcd H 12.16% C 79.06%, Found H 12.25% C 78.98%. NMR ^{1}H ($CDCl_3$) δ: 1.5–2.5 (m, broad, CH_2). IR (film): 2934, 2306, 1710 (CO), 1470.

Oxidation of Benzylic Alcohol

The mixture comprised of benzylic alcohol (10 mmol, 1.12 g), *tris* (triphenylphosphine) ruthenium (II) chloride [$RuCl_2(PPh_3)_3$] (0.4 mmol), hydroquinone (4 mmol, 220 mg), Pc[Fe]/ZrO_4 (1.4 g), DMF (3 ml), and H_2O (0.3 ml) was subjected to the same general procedure mentioned above.

Benzaldehyde: Obtained from benzyl alcohol, yield GC (95%), isolated 80%. IR (film) cm^{-1}: 1708 (νC=O); 1190; 977 (δC-H). NMR ^{1}H ($CDCl_3$) δ: 7.1–8.0 (m, 5H, H arom.); 9.9 (s, 1H, CHO).

Furane 2-carboxaldehyde: Obtained from furfuryl alcohol, yield GC (98%), isolated 85%. NMR ^{1}H ($CDCl_3$) δ: 6.7 (dd, 1H), 7.25 (d, 1H), 7.7 (d, 1H), 9.73 (s, 1H, CHO).

E-Cinnamyladehyde: Obtained from E-cinnamyl alcohol, yield GC (90%), isolated 77%. ^{1}H ($CDCl_3$) δ: 6.5 (d, 1H, CH), 6.85 (d, 1H, CH); 7.0–7.8 (m, 5H, H arom.); 9.65 (d, 1H, CHO).

E-(2-Furanyl)-3-propen-2-al: Obtained from (2-furanyl)-3-propen-2-ol, yield isolated 75%. NMR ^{1}H ($CDCl_3$) δ: 6.5 (d, 1H, CH), 6.85 (d, 1H, CH); 7.0–7.8 (m, 5H, H arom.); 9.75 (d, 1H, CHO).

Diacetoxylation of 1,3-Cyclohexadiene

We added successively in a 50 ml flask, the supported phthalocyanine Pc[Fe]/$ZrPO_4$ (1 g), $Pd(OAc)_2$ (0.14 mmol, 0.032 g), LiOAc (1.37 mmol, 0.14 g), the hydroquinone (0.28 mmol, 0.04 g) and, finally, acetic acid (5 ml). Finally the 1,3-cyclohexadiene (1.5 mmol, 120 mg) in hexane (5 ml) was added. Oxygen was bubbled through the mixture stirred at room temperature for 24 h. After filtration, the organic layer was recovered. The aqueous layer was diluted in aqueous saturated solution of sodium chloride (3 ml) and then extracted with a solution of hexane/ether (1 : 1) (3 × 10 ml).

The combined organic layers were washed successively with an aqueous saturated solution of sodium chloride (3 × 3 ml), with water (3 × 3 ml) and with soda 2 M (3 × 5 ml) and were then dried over magnesium sulfate and evaporated under reduced pressure.

1,4-Diacetoxy-2-cyclohexene (mixture of *trans* and *cis*): Yield isolated 50%, $C_{10}H_{14}O_4$. Calcd H 7.12% C 60.59%, Found H 7.23% C 60.28%. IR (film) cm^{-1}: 2926, 1730, 1652, 1436, 1370, 1138, 916. NMR ^1H ($CDCl_3$) δ: 1.7–2.21 (m, 6H, CH_2); 2.04 (s, 6H, CH_3); 5.30 and 5.17 (m, 2H, CHOAc); 5.9 (m, 2H, CH=). The product is a mixture of isomers[18] (estimation from NMR: *trans/cis* about 9).

REFERENCES

1. Snider, B.; Amin, S.G. Synth. Commun. **1978**, *8*, 117; Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. Helv. Chim. Acta **1945**, *42*, 195.
2. Muchie, J.K.; Miller, J.A. Synthesis **1981**, 824.
3. Kochhar, K.S.; Bal, B.S.; Deshpande, R.P.; Rajadhyakha, S.N.; Pinnic, H.W. J. Org. Chem. **1983**, *48*, 1785.
4. Clark, J.H. Ed. *Chemistry of Waste Minimisation*. Chapman and Hall: London, 1995.
5. Prahov, L.T.; Andreev, A.A. React. Kinet. Catal. Lett. **1975**, *3*, 315.
6. Campadelli, F.; Cariati, F.; Carniti, P.; Morazzoni, F.; Ragaini, V.J. Catal. **1967**, *44*, 167; Mercati, G.; Morazzoni, F. Inorg. Chim. Acta **1977**, *25*, 1115; Homeier, E.H.; Johnson, R.W. US-Patent **1980**, 455, 4, 234; Chem. Abst. **1981**, *94*, 37141; Mercati, G.; Morazzoni, F.; Barzaghi, M.; Carniti, P.; Ragaini, V.; Campadelli, F. J. Chem. Soc. Faraday Trans. I **1979**, *8*, 1857.
7. Diegruber, F.; Plath, P.J. Stud. Surf. Sci. Catal. **1982**, *12*, 23; Diegruber, H.; Plath, P.J. Z. Phys. Chem. **1985**, *266*, S 641.
8. Fujitsu, H.; Sakakihara, T.; Mochida, I. Chem. Lett. **1991**, 159.
9. Appleby, A.J.; Savy, M. Electrochim. Acta **1976**, *21*, 567; Veen, J.A.R.; Visser, C. Electrochim. Acta **1979**, *24*, 921; Yamada, M.; Dasby, R.; White, R.E. Electrochim. Acta **1984**, *29*, 329.
10. Bram, G.; Loupy, A.; Villemin, D. In *Solid Supports and Catalysts in Organic Synthesis*; Chap. 12, p. 302–326, Smith, K., Ed., Ellis Horwood and Prentice Hall, 1992. Hammadi, M. Ph.D. thesis, University of Caen 1996. Villemin, D.; Hammadi, M. Actes du 3 èmeColloque Franco-Maghrebin de Catalyse, CFMC, 611, 1996.
11. Meyer, G.; Wöhrle, D.; Mohl, M.; Schulz-Ekloff, G. Zeolites **1984**, *4*, 30.

12. Cook, A.H. J. Chem. Soc. **1938**, 1768; Bäckvall, J.E.; Hopkins, R.B.; Grennberg, H.; Mader, M.M.; Awasthi, A.K. J. Amer. Chem. Soc. **1990**, *112*, 5160; Zsigmond, A.; Notheisz, F.; Bäckvall, J. E. Cat. Lett. **2000**, *65*, 135.
13. Elbs, K. J. Prakt. Chem. **1993**, *48*, 179.
14. Combes, A. Bull. Soc. Chim. **1907**, *1*, 800; Soderquist, C.J. J. Chem. Ed. **1973**, *50*, 782.
15. Windholz, M. Ed. *The Merck Index*, 12th Ed.; Merck and Co.: Rahway, USA, 1983.
16. Villemin, D.; Bar, N.; Hammadi, M. Tetrahedron Lett. **1997**, *38*, 4777.
17. Fieser, L. J. Biol. Chem. **1940**, *133*, 391.
18. Bäckvall, J.E.; Byström, S.E.; Nordberg, R.E. J. Org. Chem. **1984**, *49*, 4619; Bäckvall, J.E.; Awasthi, A.K.; Renko, Z.D. J. Amer. Chem. Soc. **1987**, *109*, 4750; Bäckvall, J.E.; Vagberg, J. J. Org. Chem. **1988**, *53*, 5695; Bäckvall, J. E.; Bruce, R.E. Tetrahedron Lett. **1988**, *29*, 2885; Bäckvall, J.E.; Chowdhury, R.L.; Karisson, U.R. J. Chem. Soc. Chem. Comm. **1991**, 473; Aranyos, A.; Szabo, K.J.; Bäckvall, J.E. J. Org. Chem. **1998**, *63*, 2523.
19. Holm, R. Inorg. Synth. *13*, 239.

Received in the UK February 8, 2001

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016