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Dimethyl carbonate: an environmentally friendly solvent for hydrogen peroxide (H_2O_2)/methyltrioxorhenium (CH_3ReO_3, MTO) catalytic oxidations

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Abstract—Environmentally friendly oxidations of various organic compounds with the hydrogen peroxide (H_2O_2)/methyltrioxorhenium (CH_3ReO_3, MTO) catalytic system have been described in dimethyl carbonate (DMC), a cheap commercially available and benign chemical having interesting solvating properties, low toxicity and high biodegradability. Oxidations proceeded with good conversions and in good yields. Spectrophotometric analysis demonstrated that the [$CH_3ReO(O–O)_2$] complex was formed in DMC and that it was stable for several days at room temperature.

1. Introduction

Oxidations of organic compounds are very useful reactions in the fine-chemicals industry. Stoichiometric oxidants such as chromium(VI) salts, ceric ammonium nitrate (CAN), nitric acid, thallium (III) nitrate, hypervalent iodine(III), dipotassium nitrosodisulfonate (Fremy's salt), potassium permanganate, silver(I) oxide/nitric acid and *m*-chloroperbenzoic acid have been widely employed in the past. However, these systems have drawbacks due to their toxicity, high reaction temperature and use of acidic or basic conditions.[1]

In recent years, increasingly stringent environmental requirements have led to a great interest in the application of sustainable and green oxidations. Convenient and environmentally friendly oxygen atom donors such as molecular oxygen and hydrogen peroxide have attracted considerable attention. In particular, the role of hydrogen peroxide in organic synthesis has grown steadily over the years.[2] The use of this oxidant is particularly attractive, both for its high oxygen content and the formation of water as a byproduct. Moreover, diluted aqueous solutions of hydrogen peroxide are stable and they can be easily handled and stored. Catalysts known to activate hydrogen peroxide include: iron and manganese porphyrins,[3] phthalocyanines,[4] iron amide complexes,[5] TAML,[6] selenoxides,[7] polyoxometallates,[8] titanium silicalite,[9] tungsten, molybdenum and vanadium complexes[10] and Sn-zeolite beta.[11]

During the last decade, a large number of scientific papers have been published about the use of an organometallic rhenium compound, methyltrioxorhenium (CH_3ReO_3, MTO) **1**, as efficient activator for hydrogen peroxide.[12] At room temperature, it is a colourless solid, thermally stable to 300 °C and soluble in many organic solvents[13] and in ionic liquids.[14]

MTO was first synthesized in a small scale (milligrams)[15] but successively more efficient synthetic procedures have been reported.[16] Recently, a new large-scale (until 1200 g) and economically advantageous synthesis of MTO has been described.[17]

The mechanism of MTO-catalyzed oxidations is based on the formation of two peroxo complexes of stoichiometry [$CH_3ReO_2(O–O)$] **2** and [$CH_3ReO(O–O)_2$] **3** (Scheme 1). Experiments with the isolated complex **3** have shown that it is the active species in oxidation catalysis. In contrast, the complex **2** has never been isolated and exists only in equilibrium with MTO and **3**.[18]

Keywords: Dimethyl carbonate; Green oxidations; Hydrogen peroxide (H_2O_2)/methyltrioxorhenium (CH_3ReO_3, MTO).

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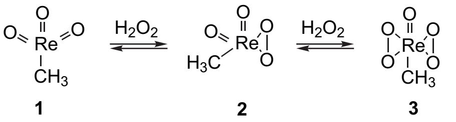

Scheme 1. The hydrogen peroxide/methyltrioxorhenium catalytic system.

The hydrogen peroxide/methyltrioxorhenium catalytic system has been widely used in a variety of synthetic transformations.[12] Our research group has performed oxidative modifications of natural organic compounds to obtain bioactive compounds.[19] Recently, we have investigated these reactions in alternative solvents such as ionic liquids.[20–22] Continuing our research with the aim to lower the environmental impact of these oxidations, we turned our attention to dimethyl carbonate (DMC), a chemical produced through a green catalytic process by Enichem (Italy).[23] Its low toxicity, the absence of irritating or mutagenic effects associated with it and its high biodegradability qualify DMC as an environmentally friendly chemical (Table 1).[24]

As extensively reported by Tundo et al.,[25] in organic synthesis, DMC is a well known reagent used as benign substitute for hazardous and toxic reagents such as dimethyl sulfate, methyl iodide and phosgene. In fact, in the presence of a nucleophile and in basic conditions, DMC exhibits a versatile and tunable chemical reactivity, depending on the experimental conditions. In particular, at the reflux temperature (90 °C), it can react as a methoxycarbonylating agent; at $T>120$ °C (usually $T=160$ °C) it acts as a methylating reagent. Both reactions generate methanol as byproduct that can be recycled for the same production of DMC,[26] avoiding the formation of unwanted inorganic salts and the related disposal problems.

In biocatalysis, a chemoenzymatic epoxidation of alkenes with DMC and hydrogen peroxide has been reported.[27] A monoperoxy carbonic acid methyl ester was generated in situ under neutral conditions by lipase-catalyzed perhydrolysis of dimethyl carbonate with hydrogen peroxide. Blank experiments without enzyme gave no measurable amount of this species. Furthermore, DMC has found many industrial applications in the field of natural leather coating, metal cleaning, degreasing in textiles and tanning and polymer coating.[28] In the pharmaceutical industry, it is used as an extraction solvent replacing toluene.

To the best of our knowledge, only palladium-catalyzed cyclocarbonylation reactions[29] and ruthenium tetraoxide oxidations[30] has been performed in DMC, as a reaction medium, in organic synthesis. In this paper we investigated the applicability of the hydrogen peroxide/methyltrioxorhenium catalytic system using DMC as solvent for the oxidation of a wide range of organic compounds.

Table 1. Toxicological and ecotoxicological properties of DMC[23]

Property	Value
Oral acute toxicity (rats)	LD_{50} 13.8 g/kg
Acute toxicity per contact (cavy)	$LD_{50}>2.5$ g/kg
Acute toxicity per inhalation (rats)	LC_{50} 140 mg/L (4 h)
Mutagenic properties	None
Irritating properties (rabbits, eyes, skin)	None
Biodegradability	>90% (28 days)
Acute toxicity (fish)	NOEC[a] 1000 mg/L
Acute toxicity on aerobic bacteria of wastewaters	$EC_{50}>1000$ mg/L

[a] NOEC=concentration, which does not produce any effect.

2. Results and discussion

Before investigating the oxidation reactions, the formation and the stability of the diperoxo complex $[CH_3ReO(O–O)_2]$ **3** in DMC have been evaluated. We performed these studies by conventional UV–vis spectroscopy. On treatment of MTO in DMC with an excess of hydrogen peroxide (35% water solution), a yellow solution was obtained. As in other organic solvents[31] and in ionic liquids,[14] the maximum of absorbance at $\lambda=360$ nm ($\varepsilon=1186\ M^{-1}\ cm^{-1}$) can be attributed to the diperoxo complex **3** (Fig. 1). Spectrophotometric determinations of absorbance at this fixed wavelength confirmed that the complex **3** is stable for several days at room temperature. Probably, the DMC, a highly oxygenated compound, has the ability to complex and to stabilize the methyltrioxorhenium catalyst.

After verifying the stability of the diperoxo complex, we investigated the oxidation reactions of different model organic compounds using the H_2O_2/CH_3ReO_3 catalytic system in DMC as solvent. Experimental conditions and results of the reactions are shown in Table 2. All substrates are soluble in DMC. When the oxidations were carried out under identical conditions but omitting the catalyst, products were formed only in traces (<5%).

MTO has been successfully described as an efficient olefin epoxidation catalyst. Its reactivity in this oxidation depends on several factors such as the polarity of the solvent and the presence of an appropriate amount of heterocyclic base (pyridine,[32] 3-cyanopyridine,[33] pyrazole[34]). We epoxidized styrene in DMC as an example (Table 2, entry 1). The alkene was added to a solution of urea hydrogen peroxide adduct (UHP)/methyltrioxorhenium in DMC at room temperature. After 16 h, styrene oxide was obtained in quantitative conversion and yield. No heterocyclic bases were needed to increase the selectivity of the oxidation and to modulate the activity of the catalyst. The conversion and yield were similar to the oxidation performed in an ionic liquid solution[35] but a lower amount of the catalyst was used with DMC as solvent.

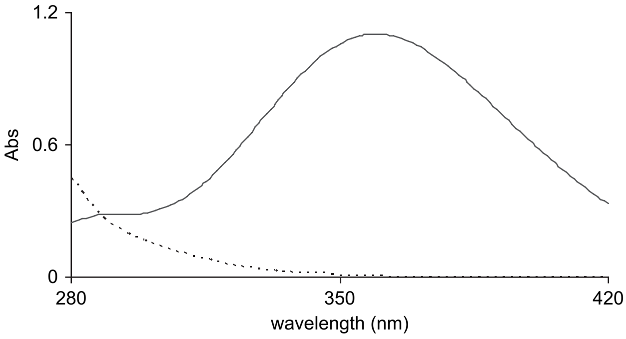

Figure 1. UV–vis spectrum of MTO **1** (- - - -) and of diperoxo complex **3** (—) in DMC. Conditions: 0.93 mM MTO, 42 mM H_2O_2, room temperature.

Table 2. Catalytic oxidations with hydrogen peroxide (H_2O_2)/methyltrioxorhenium (CH_3ReO_3) in DMC as solvent

Entry	Starting material	Experimental conditions	Conv. (%)[a]	Products (yield %)[a]
1	Styrene	UHP (2 equiv), MTO (0.5%), rt, 16 h	>98	Styrene oxide (>98)
2	2,3-Dimethylnaphthalene	H_2O_2 (10 equiv), MTO (5%), 60 °C, 20 h	>98	2,3-Dimethyl-1,4-naphthoquinone (>98)
3	3,5-Dimethylphenol	H_2O_2 (3 equiv), MTO (2%), 60 °C, 7 h	>98	2,6-Dimethyl-1,4-benzoquinone (80)
4	Diphenylmethanol	H_2O_2 (2 equiv), MTO (5%), rt, 4.5 h	>98	Benzophenone (60)
5	Diphenyl sulfide	H_2O_2 (1 equiv), MTO (1%), 50 °C, 3 h	>98	Diphenyl sulfoxide (90) Diphenyl sulfone (10)
6	*p*-Hydroxybenzaldehyde	H_2O_2 (2 equiv), MTO (2%), 50 °C, 2.5 h	>98	Hydroquinone (75) *p*-Benzoquinone (25)
7	Adamantanone	H_2O_2 (2 equiv), MTO (2%), 60 °C, 3.5 h	>98	4-Oxohomoadamantan-5-one (>98)

[a] GC–MS conversions and yields.

The oxidation of arenes with hydrogen peroxide/methyltrioxorhenium was generally performed in glacial acetic acid[36] or acetic acid/acetic anhydride,[37] with concentrated (85%) hydrogen peroxide and at elevated temperatures. In a neutral solvent such as DMC, 2,3-dimethylnaphthalene was quantitatively converted into the corresponding 2,3-dimethyl-1,4-naphthoquinone after 20 h with MTO and an excess of hydrogen peroxide 35% water solution (Table 2, entry 2).

Acetic acid and concentrated hydrogen peroxide[38] was also required to oxidize phenols, by the homogeneous hydrogen peroxide/methyltrioxorhenium catalytic system, to the corresponding *p*-benzoquinones. In DMC as solvent, the oxidation of 3,5-dimethylphenol gave in high conversion (>98%) and good yield (80%) the corresponding 2,6-dimethyl-1,4-benzoquinone with 3 equiv of hydrogen peroxide and MTO (Table 2, entry 3). Conversion and yield are increased compared to acidic conditions.[39]

The oxygen atom insertion into the C–H bond of hydrocarbon derivatives catalyzed by the homogeneous hydrogen peroxide/methyltrioxorhenium catalytic system proceeded in ethanol or in *t*-butanol.[39] Generally, long reaction times were needed (24–72 h). We observed that in DMC the catalytic conversion of diphenylmethanol, as a substrate model, to benzophenone proceeded at room temperature with only 2 equiv of hydrogen peroxide, a low percent of MTO and a short reaction time (4.5 h, Table 2, entry 4).

The oxidation of sulfides to sulfoxides by hydrogen peroxide under methyltrioxorhenium catalysis was performed with concentrated hydrogen peroxide (85% water solution) in about 24 h.[40] Diphenyl sulfide was oxidized in DMC to the corresponding sulfoxide in 90% yield after only 3 h, with 1 equiv of diluted hydrogen peroxide solution (35% water solution) and a low amount of MTO (Table 2, entry 5). The diphenyl sulfone was obtained in low yield (10%).

Oxidative synthesis of phenols from *o*,*p*-hydroxy or *o*,*p*-methoxybenzaldehydes has been performed in traditional solvents[41] and in ionic liquids solution.[21] *p*-Hydroxybenzaldehyde in DMC was converted into the corresponding hydroquinone (yield: 75%) and *p*-benzoquinone (yield: 25%). Oxidation proceeded in a short reaction time (2.5 h) and with a low amount of catalyst (Table 2, entry 6).

MTO catalyzes the Bayer–Villiger reaction of cyclic ketones to the corresponding lactones.[20,42] In DMC, 2-adamantanone was quantitatively oxidized to the 4-oxohomoadamantan-5-one with MTO and a low amount of hydrogen peroxide 35% water solution (Table 2, entry 7). Reaction times are shorter than in an ionic liquid solution.[20]

After these general investigations about the efficiency of the hydrogen peroxide/methyltrioxorhenium catalytic system in DMC, we specifically focused our attention on the oxidation of alkylated phenol and methoxybenzene derivatives to obtain the corresponding *p*-benzoquinones. In fact, we recently showed that these compounds exhibit interesting antifungal activities against the growth of soil fungi such as *Trichoderma koningii*, *Paecilomyces*, *Aspergillus flavus*, *Penicillium roseopurpureum*, *Geomyces pannorum* var. *pannorum*, *Fusarium* sp. and *Pestalotia* sp. In particular, we proved that some of them are more potent inhibitors against *Fusarium* sp. than ketoconazole, a commercially available antifungal agent.[22] Experimental results are reported in Table 3. All starting phenol and methoxybenzene derivatives are soluble in DMC and were converted to the corresponding *p*-benzoquinones in 4–24 h. Conversions and yields are higher than in acetic acid[34] and similar to those obtained

Table 3. Catalytic oxidations of phenols and methoxytoluenes with hydrogen peroxide (H_2O_2)/methyltrioxorhenium (CH_3ReO_3) in DMC as solvent

Entry	Starting material	Experimental conditions	Conv. (%)[a]	Products (yield %)[a]
1	2,3,5-Trimethylphenol	H_2O_2 (4 equiv), MTO (2%), 60 °C, 7 h	>98	2,3,5-Trimethyl-1,4-benzoquinone (95)
2	2,3,6-Trimethylphenol	H_2O_2 (4 equiv), MTO (2%), 60 °C, 7 h	>98	2,3,5-Trimethyl-1,4-benzoquinone (>98)
3	2-*t*-Butyl-5-methylphenol	H_2O_2 (8 equiv), MTO (2%), 60 °C, 7 h	>98	2-*t*-Butyl-5-methyl-1,4-benzoquinone (>98)
4	2-*t*-Butyl-6-methylphenol	H_2O_2 (6 equiv), MTO (2%), 60 °C, 4 h	>98	2-*t*-Butyl-6-methyl-1,4-benzoquinone (95)
5	2,6-Diisopropylphenol	H_2O_2 (8 equiv), MTO (2%), 60 °C, 24 h	>98	2,6-Diisopropyl-1,4-benzoquinone (95)
6	2,6-Di-*t*-butylphenol	H_2O_2 (8 equiv), MTO (2%), 60 °C, 24 h	95	2,6-Di-*t*-butyl-1,4-benzoquinone (95)
7	1-Naphtol	H_2O_2 (6 equiv), MTO (2%), 60 °C, 6 h	>98	1,4-Naphtoquinone (90)
8	3,4-Dimethoxytoluene	H_2O_2 (10 equiv), MTO (4%), 60 °C, 6 h	>98	2-Methoxy-5-methyl-1,4-benzoquinone (80)
9	3,5-Dimethoxytoluene	H_2O_2 (10 equiv), MTO (4%), 60 °C, 6 h	>98	2-Methoxy-6-methyl-1,4-benzoquinone (75)
10	3,4,5-Trimethoxytoluene	H_2O_2 (10 equiv), MTO (4%), 60 °C, 4 h	>98	2-Methoxy-6-methyl-1,4-benzoquinone (>98)

[a] GC–MS conversions and yields.

by us in an ionic liquid solution; however, in DMC a lower amount of the catalyst is needed (2–4%).[22]

3. Conclusions

DMC, a highly oxygenated compound having good solvent properties, low toxicity and ecotoxicity, can be used as an environmentally friendly reaction medium for methyltrioxorhenium-catalyzed oxidations of a wide range of substrates. Methyltrioxorhenium and the diperoxo complex $[CH_3ReO(O–O)_2]$ **3** are soluble in DMC and this species is stable for days at room temperature. Oxidations proceed with high conversions and yields. Products are obtained after shorter reaction times than in traditional solvents and similar to those observed in ionic liquids. Using DMC as solvent, often a lower amount of catalyst is needed than with traditional solvents or ionic liquids.

4. Experimental

All commercial products were of the highest grade available and were used as such. Urea hydrogen peroxide and hydrogen peroxide 35% water solution are commercially available (Aldrich). NMR spectra were recorded on a Bruker (200 MHz) spectrometer and are reported in δ values. Gas chromatography–mass spectra (GC–MS) were recorded using a GC-17A Shimadzu gas chromatograph equipped with an electron beam of 70 eV, a SPB column (25 m×0.30 mm and 0.25 mm film thickness) and a FID as detector. The injector temperature was 280 °C. An isothermal temperature profile of 60 °C for 5 min, followed by a 10 °C/min temperature gradient to 250 °C for 5 min were used. Chromatography grade helium was used as the carrier gas. Thin layer chromatography was carried out using Merck platen Kieselgel 60 F254. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh).

4.1. Spectrophotometric analysis

Spectrophotometric analyses were performed with a Cary-4 Varian spectrometer at 25 °C. Quartz cuvettes (4 mL) with 1.0 cm optical path length were used. A solution of hydrogen peroxide/methyltrioxorhenium was prepared as reported: methyltrioxorhenium (2.78 mg, 0.011 mmol) was solubilized in DMC (12 mL), and then hydrogen peroxide 35% water solution (43.8 µL, 0.5 mmol) was added. The formation of the diperoxorhenium complex **3** was monitored by measuring the absorbance changes of this solution in the range λ=280–420 nm and by observing the formation of a maximum of absorbance at λ=360 nm. The stability of the diperoxorhenium complex was measured by monitoring the decline in absorbance at this wavelength for seven days at room temperature.

4.2. General procedure for the oxidation of organic compounds with hydrogen peroxide/methyltrioxorhenium in dimethyl carbonate

In a typical experiment, hydrogen peroxide (2.0 equiv, 35% water solution) and the substrate (1.0 mmol) to be oxidized were added to a solution of the methyltrioxorhenium (1.0% w/w) in DMC (2 mL) and the mixture was stirred at the appropriate temperature (see Tables 2 and 3). Oxidations were monitored by TLC and GC–MS analysis. Depending on the substrate, for a quantitative conversion, successive additions of hydrogen peroxide/methyltrioxorhenium were performed. At the end of the reaction, MnO_2 was added to the solution to degrade the excess of hydrogen peroxide and the reaction mixture was vigorously stirred for 15 min. After filtration, methanol was added to the solution and the azeotropic mixture (methanol:DMC=3:1 v/v) boiling at 64 °C was evaporated under vacuum.[43] The reaction products were extracted with ethyl acetate (3×20 mL) and the organic layers were dried over anhydrous sodium sulfate. The crude product was purified by preparative TLC or by flash chromatography on silica gel using dichloromethane/methanol or ethyl acetate/hexane mixtures as eluents. All the products were identified by comparison of their ^1H NMR, ^{13}C NMR and GC–MS spectra with those of authentic compounds. Styrene oxide, benzophenone, diphenyl sulfoxide, diphenyl sulfone, hydroquinone, *p*-benzoquinone, 1,4-naphthoquinone and 2-methoxy-5-methyl-1,4-benzoquinone are commercially available compounds (Sigma, Aldrich, Fluka); samples of 2,3-dimethyl-1,4-napththoquinone, 2,6-dimethyl-1,4-benzoquinone, 4-oxohomoadamantan-5-one and the other benzoquinones reported in Table 3 were prepared according to previously published procedures.[20,22] Conversions and yields of the oxidations were calculated by GC–MS analysis.

4.2.1. 2,3-Dimethyl-1,4-naphthoquinone. Yield: >98%. Yellow oil. [Found: C, 77.6; H, 17.1; O, 5.3. $C_{10}H_{14}O_2$ required C, 77.4; H, 17.2; O, 5.4%]. δ_H (200 MHz, $CDCl_3$) 2.11 (6H, s, CH_3), 7.60–7.65 (2H, CH_{ar}), 7.97–8.02 (2H, CH_{ar}). δ_C (200 MHz, $CDCl_3$) 13.5, 127.0, 133.0, 134.2, 144.2, 185.6; *m*/*z* 186 (M^+).[44]

4.2.2. 2,6-Dimethyl-1,4-benzoquinone. Yield: 80%. White solid;[45] mp 72–74 °C (lit. 71–73 °C).

4.2.3. 4-Oxohomoadamantan-5-one. Yield: >98%. Colourless oil. [Found: C, 72.5; H, 8.4; O, 19.1. $C_{10}H_{14}O_2$ required C, 72.3; H, 8.5; O, 19.2%]. δ_H (200 MHz, $CDCl_3$) 1.60–2.08 (12H, s, 5×CH_2 and 2×CH), 3.04 (1H, m, $–(CH_2)_2CHCO$), 4.46 (1H, m, $–(CH_2)_2CHO–$); δ_C (200 MHz, $CDCl_3$) 25.7, 30.8, 33.6, 35.6, 41.1, 73.4, 179.5; *m*/*z* 166 (M^+).

4.2.4. 2,3,5-Trimethyl-1,4-benzoquinone. Yield: 95%. Yellow solid;[22] mp 27–29 °C (lit.[46] 29 °C).

4.2.5. 2-*tert*-Butyl-5-methyl-1,4-benzoquinone. Yield: >98%. Yellow oil.[22] [Found: C, 74.5; H, 7.7, O, 17.8. $C_{11}H_{14}O_2$ required C, 74.1; H, 7.9; O, 18.0%]; δ_H (200 MHz, $CDCl_3$) 1.19 (9H, s, $C(CH_3)_3$, 1.96 (3H, d, *J* 1.5 Hz, CH_3), 6.46 (1H, q, *J* 1.5 Hz, $CH{=}CCH_3$), 6.52 (1H, s, $CH{=}CC(CH_3)_3$); δ_C (200 MHz, $CDCl_3$) 14.9, 29.1, 131.5, 135.9, 144.1, 156.0, 187.8, 188.9; *m*/*z* 178 (M^+).

4.2.6. 2-*tert*-Butyl-6-methyl-1,4-benzoquinone. Yield: 95%. Yellow oil.[22] [Found: C, 74.5; H, 7.6; O, 17.9. $C_{11}H_{14}O_2$ required C, 74.8; H, 7.4; O, 17.8%]; δ_H (200 MHz, $CDCl_3$) 1.10 (9H, s, $C(CH_3)_3$), 1.91 (3H, d, *J* 1.3 Hz, CH_3), 6.41 (2H, m, $CH{=}CCH_3$ and

$\mathrm{C}H{=}\mathrm{CC(CH_3)_3}$); δ_C (200 MHz, $\mathrm{CDCl_3}$) 16.1, 28.7, 131.3, 131.9, 147.6, 156.2, 187.6, 188.6; *m/z* 178 ($\mathrm{M^+}$).

4.2.7. 2,6-Diisopropyl-1,4-benzoquinone. Yield: 95%. Yellow oil.[22,47] [Found: C, 75.2; H, 8.0; O, 16.8. $\mathrm{C_{12}H_{16}O_2}$ required C, 75.0; H, 8.4; O, 16.6%]; δ_H (200 MHz, $\mathrm{CDCl_3}$) 1.14 (12H, d, $\mathrm{2CH(C}H_3\mathrm{)_2}$, 3.08 (2H, hept, *J* 6.8 Hz, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.47 (2H, s, $\mathrm{C}H{=}\mathrm{CCH(CH_3)_2}$); δ_C (200 MHz, $\mathrm{CDCl_3}$) 21.1, 27.0, 129.8, 155.3, 186.8, 188.6; *m/z* 192 ($\mathrm{M^+}$).

4.2.8. 2,6-Di-*tert*-butyl-1,4-benzoquinone. Yield: 95%. Orange solid;[22] mp 66–68 °C (lit.[48] 65–68 °C).

4.2.9. 1,4-Naphthoquinone (13). Yellow solid; mp 118–121 °C (lit.[49] 119–120 °C).

4.2.10. 2-Methoxy-6-methyl-1,4-benzoquinone. Yield: >98%. Yellow oil.[22,,50] [Found: C, 63.8; H, 5.0; O, 31.2. $\mathrm{C_8H_8O_3}$ required C, 63.2; H, 5.3; O, 31.5%]; δ_H (200 MHz, $\mathrm{CDCl_3}$) 2.00 (3H, d, *J* 1.6 Hz, $\mathrm{C}H_3$), 3.77 (3H, s, $\mathrm{OC}H_3$), 5.83 (1H, s, $\mathrm{C}H{=}\mathrm{COCH_3}$), 6.48 (1H, q, *J* 1.6 Hz, $\mathrm{C}H{=}\mathrm{CCH_3}$); δ_C (200 MHz, $\mathrm{CDCl_3}$) 15.0, 56.3, 107.2, 133.8, 142.1, 158.0, 181.0, 186.2; *m/z* 152 ($\mathrm{M^+}$).

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