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RUTHENIUM-CATALYZED OXIDATION OF ALCOHOLS AND CATECHOLS USING t-BUTYL HYDROPEROXIDE

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Summary

Ruthenium complexes catalyze the oxidation of alcohols to the corresponding ketones or aldehydes when t-BuOOH (70% aq.) is used as an oxidant. The reactions proceed at room temperature to give the products in excellent to fairly good yields. Among the transition metal catalysts used, dichlorotris(triphenylphosphine)-ruthenium ($RuCl_2(PPh_3)_3$) showed the highest catalytic activity. 3,5-Di-t-butylcatechol and 4-t-butylcatechol are also effectively oxidized to the corresponding 1,2-benzoquinones in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ at room temperature with 1.1 equiv. of t-BuOOH, in quantitative yields. Hydrogen peroxide (30% aq.) can also be employed as an oxidant to give 1,2-benzoquinones in excellent yields.

Introduction

The preparation of carbonyl compounds by the oxidation of alcohols is of great value in organic synthesis. Transition metal-catalyzed oxidation of alcohols is of current interest, and various transition metal compounds and oxidant systems have been reported [1].

Unsaturated organic compounds were used as oxidants in the presence of ruthenium or rhodium compounds [2]. Ruthenium and palladium complexes are useful catalysts in the oxidation of alcohols, using halogenated compounds such as bromobenzene [3] and carbon tetrachloride [4] as oxidants. Ruthenium compounds combined with a molecular oxygen system are also effective for the oxidation of alcohols, especially conjugated alcohols [5]. In these reactions, however, a long reaction time and/or a rather high temperature were required. Muller and Goday have also reported that iodosylbenzene in conjunction with ruthenium catalysts is an efficient oxidant for the conversion of alcohols to carbonyl compounds [6].

Sharpless et al. have extensively investigated the effectiveness of a wide variety of

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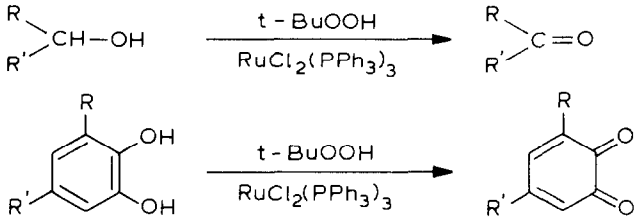
transition metal and oxidant systems, and concluded that the combination of a $RuCl_2(PPh_3)_3$ with an amine-*N*-oxide pair was most effective [7]. They also examined the activity of t-butyl hydroperoxide (t-BuOOH) as an oxidant, but claimed that although the employment of the peroxide realized some success its activity was much lower than that of the amine-*N*-oxide [7]. We have recently investigated the activation of alcohols with ruthenium catalysts: allylic alcohols–aminoarenes or aliphatic alcohols–nitroarenes systems gave quinoline derivatives in the presence of $RuCl_2(PPh_3)_3$, and aliphatic alcohols reacted with aminoarenes or amides to give *N*-alkylaminoarenes or *N*-alkylamides in the presence of $RuCl_2(PPh_3)_3$ [8]. The above statement of Sharpless et al. prompted us to reinvestigate the catalytic oxidation with t-BuOOH towards a hydroxyl function.

In this paper, we wish to report the ruthenium-catalyzed oxidation of alcohols or catechols using t-BuOOH as an oxidant. The peroxide, inexpensive and easy to handle, shows high reactivity in the presence of several ruthenium catalysts. The present procedure provides a simple method of converting alcohols to the corresponding ketones or aldehydes (eq. 1), and catechols to 1,2-benzoquinones (eq. 2) in high yields.



Results and discussion

Oxidation of alcohols

Alcohols were converted to the corresponding carbonyl compounds by t-BuOOH in the presence of $RuCl_2(PPh_3)_3$ at room temperature (Table 1). 1-Phenylethanol was oxidized to acetophenone in an almost quantitative yield in acetone (Run 1). The oxidation proceeded with very low turnovers in the absence of t-BuOOH (Run 2) [9]. Benzene and dioxane can be used as solvents (Runs 3, 5 and 10) but in the THF medium, conversion of the alcohol decreased considerably (Run 8). Under these conditions (at room temperature for 3 h), excess t-BuOOH favored a high conversion of secondary alcohols (Runs 4–6). On the other hand, in the case of primary alcohols (Runs 14–20), excess t-BuOOH reduced selectivity to aldehydes and oxidized the aldehydes formed to carboxylic acids. The high selectivity to the aldehyde is attained by a short contact time with the oxidant (Run 16) or by lowering the reaction temperature (Run 19). Geraniol was oxidized to geranial (Run 20). In this transformation, isomeric neral was not detected by GLC analysis, indicating that the configuration of the double bond was not affected during the oxidation.

In order to compare the relative rates of the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds, a competitive oxidation of benzyl alcohol with 1-phenylethanol was examined. At 0 °C, t-BuOOH (15 mmol)

was added to a mixture of benzyl alcohol (10 mmol), 1-phenylethanol (10 mmol), acetone (12 ml) and $RuCl_2(PPh_3)_3$ (0.10 mmol). After 10 min, GLC analysis of the above mixture showed the presence of benzyl alcohol (1.7 mmol), benzaldehyde (6.2 mmol), 1-phenylethanol (7.2 mmol) and acetophenone (2.8 mmol). This result indicates that the primary alcohol is oxidized much faster than the secondary one in this oxidation system.

Oxidation of catechols

The present oxidation system also shows a high activity for the conversion of catechols to 1,2-benzoquinone derivatives (Table 2). The oxidation of 3,5-di-t-butylcatechol (DTBC) at room temperature in benzene or acetone gave 3,5-di-t-butyl-1,2-benzoquinone (DTBQ) in the same yield (Runs 21, 23 and 24). When the reaction temperature was lowered to 0 °C, an almost quantitative yield was realized

TABLE 1

RUTHENIUM-CATALYZED OXIDATION OF ALCOHOLS BY t-BuOOH [a]

Run	Alcohol	Solvent	Conversion of alcohol (%) [b]	Products	Selectivity to product (%) [c]
1	1-Phenylethanol	Acetone	99	Acetophenone	100
2 [d]	1-Phenylehtanol	Acetone	5	Acetophenone	100
3	1-Phenylethanol	Benzene	89	Acetophenone	99
4 [e]	1-Phenylethanol	Dioxane	45	Acetophenone	100
5	1-Phenylethanol	Dioxane	83	Acetophenone	100
6 [f]	1-Phenylethanol	Dioxane	90	Acetophenone	99
7 [g]	1-Phenylethanol	Dioxane	56	Acetophenone	100
8	1-Phenylethanol	THF	48	Acetophenone	98
9	Cyclododecanol	Acetone	78	Cyclododecanone	69
10	Cyclododecanol	Dioxane	73	Cyclododecanone	82
11 [h]	Cyclohexanol	Acetone	82	Cyclohexanone	87
12 [i]	Cyclohexanol	Acetone	89	Cyclohexanone	74
13	2-Octanol	Acetone	58	2-Octanone	100
14 [e]	1-Octanol	Acetone	55	Octanal	58
				Octanoic acid	38
15	1-Octanol	Acetone	92	Octanal	5
				Octanoic acid	71
16 [e,j]	Benzyl alcohol	Acetone	62	Benzaldehyde	98
				Benzoic acid	<1
17	Benzyl alcohol	Acetone	99	Benzaldehyde	48
				Benzoic acid	51
18 [e,k]	Benzyl alcohol	Acetone	62	Benzaldehyde	73
				Benzoic acid	24
19 [e,l]	Benzyl alcohol	Acetone	68	Benzaldehyde	82
				Benzoic acid	16
20 [e,m]	Geraniol	Acetone	73	Geranial [n]	88

[a] To a mixture of the alcohol (10 mmol), solvent (12 ml) and $RuCl_2(PPh_3)_3$ (0.10 mmol), t-BuOOH (20 mmol; 70% aq.) was added dropwise over 1 h and the solution was stirred further for 2 h at room temperature. [b] Determined by GLC based on the amount of alcohol used. [c] Determined by GLC based on the conversion of alcohol. [d] No oxidant was used. [e] t-BuOOH (10 mmol) was used. [f] t-BuOOH (40 mmol) was used. [g] Total reaction time, 1.5 h. [h] t-BuOOH (30 mmol) was used. [i] Total reaction time, 24 h. [j] Total reaction time, 10 min. [k] At 50 °C. [l] At 0 °C. [m] Total reaction time, 4 h. [n] Without isomerization to neral.

in benzene (Run 22), while the yield was substantially decreased in acetone (Run 25). The use of dioxane, THF and acetonitrile as solvents reduced the yields of DTBQ considerably (Runs 26–28).

The oxidation of 4-t-butylcatechol (TBC) required a longer reaction time than that of DTBC. TBC was oxidized to 4-t-butyl-1,2-benzoquinone (TBQ) in acetone in 74% yield and the oxidation was complete after 18 h to give TBQ quantitatively (Runs 29 and 30). The yield of TBQ was 34% in dioxane (Run 31). However, TBC was not oxidized in benzene (Run 32), while DTBC could be readily oxidized quantitatively in this medium (Runs 21 and 22). Since the reaction mixtures in benzene were emulsions, these striking differences were attributed to differences in the solubilities of these two substrates in water and the benzene phase. The oxidation of 4-methylcatechol was reluctant to proceed by this procedure.

The oxidation of catechol to muconic acid derivatives has been investigated intensively in connection with the catalysis of pyrocatechase [10]; however, these reactions were not selective in generating several products. On the other hand, the selective oxidation of catechols to 1,2-benzoquinones was investigated using various oxidant systems, such as Ag_2CO_3/Celite [11], *N*-chlorosuccinimide/Me_2S [12], $O_2/CuCl_2/Et_3N$ [13], and $O_2/FeCl_3/SiO_2$ [14]. The latter two systems were catalytic but their catalytic activities were rather low. 1,2-Benzoquinones are important reactive intermediates for several organic syntheses [15].

Our procedure for the oxidation of catechols has several advantages: (a) quantitative yields of 1,2-benzoquinones and selective oxidation; (b) utilization of less expensive peroxide; (c) employment of only 1.1 equiv. of oxidant; (d) a high catalytic activity (highest turnover 384); and (e) mild reaction conditions.

Effect of the catalyst system

We examined the catalytic activities of several transition metal complexes in the

TABLE 2

RUTHENIUM-CATALYZED OXIDATION OF CATECHOLS USING t-BuOOH [a]

Run	Catechol	Solvent	Reaction temperature (°C)	Reaction time (h)	Product	Yield of product (%) [b]
21	DTBC [c]	Benzene	r.t	3	DTBQ [d]	92
22	DTBC	Benzene	0	3	DTBQ	100
23	DTBC	Acetone	r.t.	3	DTBQ	92
24 [e]	DTBC	Acetone	r.t.	3	DTBQ	92
25	DTBC	Acetone	0	3	DTBQ	71
26	DTBC	Dioxane	r.t.	3	DTBQ	56
27	DTBC	THF	r.t.	3	DTBQ	37
28	DTBC	Acetonitrile	r.t.	3	DTBQ	33
29	TBC [f]	Acetone	r.t.	5	TBQ [g]	74
30	TBC	Acetone	r.t.	18	TBQ	100
31	TBC	Dioxane	r.t.	24	TBQ	34
32	TBC	Benzene	r.t.	24	TBQ	0 [h]

[a] To a stirred mixture of the catechol (2.0 mmol), sovent (6 ml) and $RuCl_2(PPh_3)_3$ (0.02 mmol), t-BuOOH (2.2 mmol) was added dropwise over 1 h and the solution was stirred further for 2 h. [b] Determined by HPLC based on the amount of catechol used. [c] DTBC, 3,5-di-t-butylcatechol. [d] DTBQ, 3,5-di-t-butyl-1,2-benzoquinone. [e] t-BuOOH (3.6 mmol) was used. [f] TBC, 4-t-butylcatechol. [g] TBQ, 4-t-butyl-1,2-benzoquinone. [h] TBC was recovered almost quantitatively.

TABLE 3

OXIDATION OF CYCLOHEXANOL WITH VARIOUS CATALYSTS [a]

Run	Catalyst	Conversion of cyclohexanol (%) [b]	Selectivity to cyclohexanone (%) [c]
11	$RuCl_2(PPh_3)_3$	82	80
33	$PtCl_2(PhCN)_2$	30	97
34	$Fe(CO)_5$	27	89
35	$RhCl(CO)(PPh_3)_2$	13	100
36	$Pd(PPh_3)_4$	14	93
37	$Co(acac)_2$	13	92
38	$RhCl_3 \cdot 3H_2O$	11	91
39	$FeSO_4 \cdot 7H_2O$	11	64
40	No catalyst	7	71
41	$CoCl_2 \cdot 6H_2O$	5	100
42	$NiCl_2 \cdot 6H_2O$	6	83
43	$Ni(acac)_2$	9	44

[a] To a mixture of cyclohexanol (10 mmol), acetone (20 ml) and catalyst (0.1 mmol), t-BuOOH (20 mmol) was added dropwise over 1 h and the resulting solution was stirred for 2 h at room temperature. [b] Determined by GLC based on the amount of cyclohexanol used. [c] Determined by GLC based on the conversion of cyclohexanol.

oxidation of cyclohexanol with t-BuOOH (Table 3). $RuCl_2(PPh_3)_3$ showed the highest catalytic activity of the complexes employed. Tables 4 and 5 describe the results of the oxidation of alcohols and DTBC in the presence of several ruthenium compounds. Among them, $RuCl_2(PPh_3)_3$ was the most active (Runs 1 and 23), and the catalytic activites were maintained even in quite a low catalyst concentration (0.1 mol%, 0.05 mol% based on the substrates) (Runs 44, 45, 51–54). In the reaction of 1-phenylethanol, $RuHCl(PPh_3)_3$, $RuH_2(PPh_3)_4$ and $RuCl_3 \cdot nH_2O$ showed fairly good catalytic activities. RuO_2 had no catalytic activity in our procedure (Runs 49

TABLE 4

OXIDATION OF ALCOHOLS USING t-BuOOH; CATALYTIC ACTIVITIES OF SEVERAL RUTHENIUM COMPOUNDS [a]

Run	Alcohol	Catalyst	Amount (mmol)	Conversion of alcohol (%) [b]	Selectivity to ketone (%) [c]
1	1-Phenylethanol	$RuCl_2(PPh_3)_3$	0.10	99	100
44	1-Phenylethanol	$RuCl_2(PPh_3)_3$	0.025	99	100
45	1-Phenylethanol	$RuCl_2(PPh_3)_3$	0.010	92	100
46	1-Phenylethanol	$RuHCl(PPh_3)_3$	0.10	98	100
47	1-Phenylethanol	$RuH_2(PPh_3)_4$	0.10	95	100
48	1-Phenylethanol	$RuCl_3 \cdot nH_2O$	0.10	96	96
49	1-Phenylethanol	RuO_2	0.10	37	78
11	Cyclohexanol	$RuCl_2(PPh_3)_3$	0.10	82	80
51	Cyclohexanol	$RuCl_2(PPh_3)_3$	0.025	77	83
52	Cyclohexanol	$RuCl_2(PPh_3)_3$	0.010	71	83

[a] To a stirred mixture of the alcohol (10 mmol), acetone (12 ml) and catalyst, t-BuOOH (20 mmol) was added dropwise over 1 h and the solution was stirred further for 2 h. [b] Determined by GLC based on the amount of alcohol used. [c] Determined by GLC based on the conversion of alcohol.

TABLE 5

OXIDATION OF 3,5-DI-t-BUTYLCATECHOL USING t-BuOOH [a]: EFFECT OF RUTHENIUM CATALYST

Run	Catalyst	Amount (mmol)	Yield of DTBQ (%) [b]
23	$RuCl_2(PPh_3)_3$	0 02	92
53	$RuCl_2(PPh_3)_3$	0.002	55
54	$RuCl_2(PPh_3)_3$	0.001	48
55	$RuHCl(PPh_3)_3$	0.02	73
56	$Ru(CO)_3(PPh_3)_2$	0 02	31
57 [c]	$RuCl_3 \cdot nH_2O$	0.02	3
58 [c]	RuO_2	0.02	2

[a] To a mixture of 3,5-di-t-butylcatechol (2 mmol), acetone (6 ml) and catalyst, t-BuOOH (2.2 mmol) was added over 1 h and stirred further for 2 h at room temperature. [b] DTBQ, 3,5-di-t-butyl-1,2-benzoquinone. Determined by HPLC based on the amount of 3,5-di-t-butylcatechol used. [c] Benzene (6 ml) was used as the solvent in place of acetone.

and 58), while this compound was reported to be a good catalyst precursor in the oxidation with $NaIO_4$ or $NaClO_4$ [16].

Reaction with other oxidants

When hydrogen peroxide (30% aq.) was employed as the oxidant for the oxidation of 1-octanol, most of the hydrogen peroxide was decomposed into molecular oxygen and the yields of the carbonyl compounds were quite low (Runs 59 and 60, Table 6). On the other hand, such decomposition was not observed in the oxidation of catechols with hydrogen peroxide, and 1,2-benzoquinone derivatives were obtained in good yields (Runs 61 and 62). Di-t-butyl peroxide (DTBP) did not work as an oxidant in our procedure (Runs 63, 64 and 65). Kim and Dewhirst pointed out that the decomposition of DTBP is sluggish even at 120 °C in the presence of $RuCl_2(PPh_3)_3$ [17].

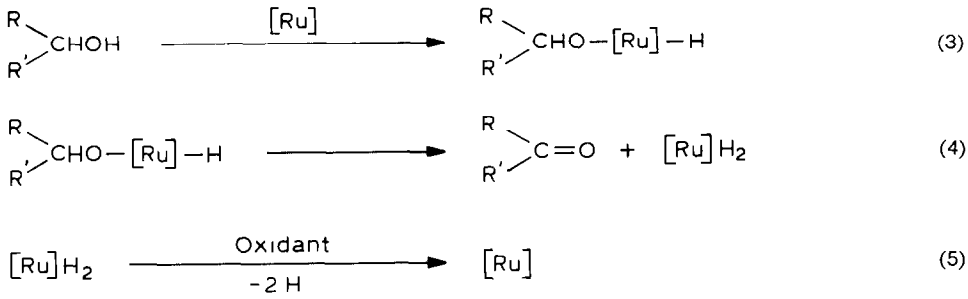
A possible mechanism for the oxidation of alcohols may be considered as follows (Scheme 1). A ruthenium alkoxide intermediate is formed via oxidative addition of the alcohol (eq. 3) and this species undergoes β-elimination to a carbonyl compound (eq. 4). Such an oxidation pathway has been proposed by several authors [18], mainly in hydrogen transfer reactions using alcohols. The alkoxohydride complex

TABLE 6

RUTHENIUM-CATALYZED OXIDATION WITH VARIOUS OXIDANTS [a]

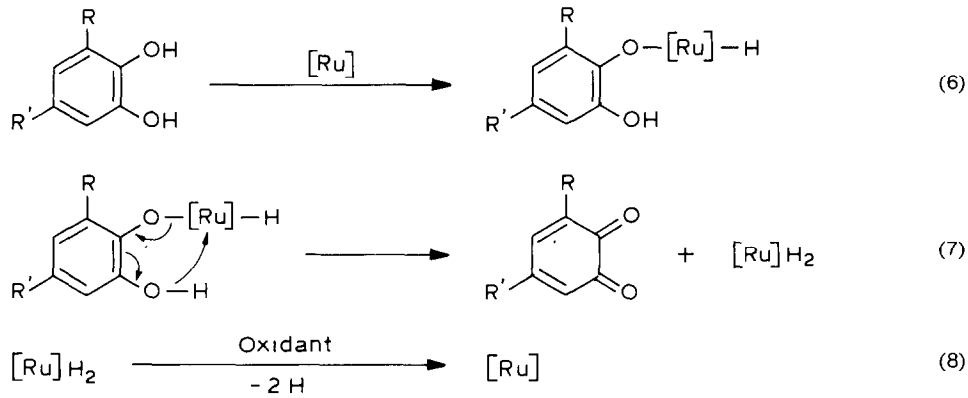
Run	Oxidant	Substrate	Product	Yield of product (%) [b]
59 [c]	H_2O_2 [d]	1-Octanol	Octanal	19
60 [e]	H_2O_2	1-Octanol	Octanal	21
61	H_2O_2	DTBC [f]	DTBQ [g]	93
62	H_2O_2	TBC [h]	TBQ [i]	88
63 [e]	DTBP [j]	1-Octanol	Octanal	3
64	DTBP	DTBC	DTBQ	Trace
65	DTBP	TBC	TBQ	Trace

[a] Oxidant/substrate/$RuCl_2(PPh_3)_3$ 1/1 1/0.01; at room temperature for 3 h in acetone. [b] Determined by GLC (octanal) or HPLC (1,2-benzoquinones). [c] In dioxane. [d] 30% aq. [e] In benzene at 0 °C. [f] DTBC, 3,5-di-t-butylcatechol. [g] DTBQ, 3,5-di-t-butyl-1,2-benzoquinone. [h] TBC, 4-t-butylcatechol. [i] TBQ, 4-t-butyl-1,2-benzoquinone. [j] DTBP, di-t-butyl peroxide.



SCHEME 1

was recently isolated as the first example in the oxidative addition of an alcohol to an alkylgermanium(II) compound [19]. The ruthenium hydride may be oxidized by t-BuOOH to regenerate the active species, and then the catalyst cycle is closed (eq. 5). For the oxidation of catechols, similar catalytic cycles could be proposed (Scheme 2).



SCHEME 2

Experimental

Materials. All substrates used were commercial products. Alcohols and catechols were purified by distillation or recrystallization before use. t-Butyl hydroperoxide (70% aq.), hydrogen peroxide (30% aq.) and di-t-butyl peroxide were used without further purification. $RuCl_2(PPh_3)_3$ [20], $RuHCl(PPh_3)_3$ [21], $RuH_2(PPh_3)_4$ [22], $Ru(CO)_3(PPh_3)_2$ [23], $RhCl(CO)(PPh_3)_2$ [24], $Pd(PPh_3)_4$ [25] and $PtCl_2(PhCN)_2$ [26] were prepared by published methods. Other transition metal compounds were used as received.

Analytical procedure. GLC analysis was carried out on a Shimadzu GC-3BT apparatus (with columns (3 mm ∅ × 3 m) packed with 20% DEGA on Uniport B 80-100 mesh or with 10% PEG 20M on Uniport B 60-80 mesh). HPLC analysis was performed on a Waters ALC/GPC 244 or on a Shimadzu LC-5A apparatus with μ-Bondapak C-18 (3.9 mm ∅ × 30 cm). A mixture of methanol and water was used as the solvent. Conversions of substrates, selectivities to the products, and the yields were determined by the internal standard method according to the calibration curves

obtained for each compound. ^{1}H NMR spectra were obtained at 100 MHz with a JEOL JNM FX-100 pulsed Fourier Transform spectrometer or at 300 MHz with a Nicolet NTC-300 spectrometer equipped with a 1180E computer system. ^{13}C NMR spectra (25.05 MHz) were measured on a JEOL JNM FX-100 pulsed Fourier Transform spectrometer. Samples were dissolved in $CDCl_3$ and the chemical shifts were expressed in relative to Me_4Si as the internal standard. IR spectra were measured on a Hitachi model 215 grating spectrophotometer.

Oxidation of alcohol. A 50 ml three-necked flask was charged with the alcohol (10 mmol), catalyst (0.10 mmol) and solvent (12 ml) under an argon atmosphere. The mixture was stirred at room temperature and t-BuOOH (10–20 mmol) was added dropwise over 1 h. The resulting dark brown solution was stirred for a further 2 h. The reaction was quenched by adding sodium sulfite (3 g). The reaction mixtures were analyzed by GLC. Reaction products were isolated by column chromatography (silica gel) and identified by comparing the spectral data (^{1}H NMR and/or ^{13}C NMR and IR spectra) and GLC retention times with those of authentic samples.

Oxidation of catechol. To a stirred mixture of the catechol (2 mmol), catalyst (0.02 mmol) and solvent (6 ml), 2.2 mmol of the oxidant was added dropwise over 1 h. The mixture was stirred magnetically for an additional 2 h. The reaction was terminated by adding 3 g of sodium sulfite. The product was isolated by medium pressure column chromatography (silica gel, Merck Art 9385-hexane/benzene/ethyl acetate). 3,5-Di-t-butyl-1,2-benzoquinone was identified by comparison of its IR [27], ^{1}H [28] and ^{13}C [29] NMR spectral data with those in the literature.

3,5-Di-t-butyl-1,2-benzoquinone. ^{13}C NMR ($CDCl_3$): δ 27.8(q,3C), 29.1(q,3C), 35.4(s), 35.9(s), 121.9(d), 133.4(d), 149.8(s), 163.1(s), 180.0(s) and 181.0(s) ppm. ^{1}H NMR ($CDCl_3$): δ 1.27(s,9H), 1.30(s,9H), 6.23(d, J 2.2 Hz) and 7.00(d, J 2.2 Hz). IR(KBr disk): 1656 cm^{-1} (ν(C=O)).

4-t-Butyl-1,2-benzoquinone. ^{13}C NMR ($CDCl_3$): δ 27.7(q,3C), 35.6(s), 123.5(d), 129.1(d), 139.7(d), 161.7(s) and 179.9(s,2C) ppm. ^{1}H NMR ($CDCl_3$): δ 1.24(s,9H), 6.28(d, J 2.2 Hz), 6.39(d, J 10.5 Hz) and 7.20(d of d, J 10.5 and 2.2 Hz). IR (KBr disk): 1652 cm^{-1} (ν(C=O)).

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