Tetrahedron Vol 44, No 20, pp 6397 to 6406, 1988
Printed in Great Britain

0040-4020/88 $3.00 + 00

COMPARATIVE OXIDATION OF PHENOLS WITH BENZENESELENINIC ANHYDRIDE AND WITH BENZENESELENINIC ACID

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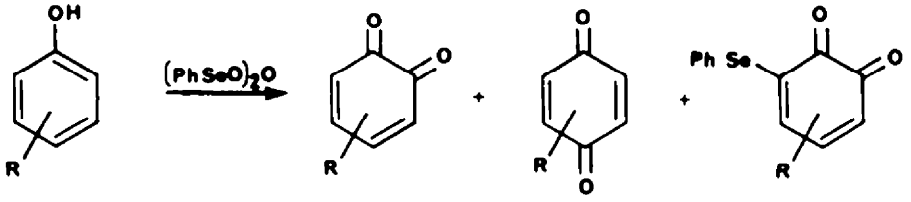
(*Received in Belgium* 29 *July* 1988)

Abstract : *Oxidation of phenols by benzeneseleninic acid* 2 *in methylene dichloride leads to the* para*-quinones, whereas oxidation by benzeneseleninic anhydride* 1 *is confirmed to afford the corresponding* ortho*-quinones. Addition of indole, as a phenylselenium (II) trapping agent, inhibits the formation of phenylselenoquinones in the oxidation with* 1 *or* 2.

The discovery of the oxidizing properties of benzeneseleninic anhydride 1 (Scheme 1) stemmed from the need for a selective oxidant to convert alkylphenols to ortho-hydroxydienones, required by the Imperial College approach to the synthesis of tetracycline[1]. A variety of methods can effect the oxidation of phenols to ortho-hydroxydienones, ortho- and para-quinones. But benzeneseleninic anhydride 1 appeared as the unique reagent for selective ortho-hydroxylation of phenols. However, two examples of preferential or selective para-quinone formation were subsequently reported[2]. The unexpected selectivity was ascribed to steric crowding and planarity distortion of the phenolic substrate. Although generally favoured, ortho-oxidation is not always selective[3]. Thus, varying amounts of para-quinones or hydroxydienones as well as phenylselenoqui-



Scheme 1

nones have been obtained. As benzeneseleninic anhydride is a moisture-sensitive compound, the presence of benzeneseleninic acid 2, also a useful oxidant[4], might influence the regioselectivity of the oxidation. The results now reported show that this hypothesis is indeed correct.

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Benzeneseleninic acid 2 was conveniently prepared by oxidation of diphenyldiselenide 3 with a stoichiometric amount of hydrogen peroxide[5]. Care must be exercised to avoid an excess of hydrogen peroxide, leading to the formation of the explosive benzeneperoxyseleninic acid[6].

Different factors were found to play a rôle on the regioselectivity of the oxidation of phenols by 1 and 2 : the nature of the oxidant, the solvent, the pH and water (Table 1).

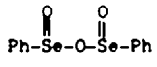
Table 1 - Oxidation of 3,5-Di-tert-butylphenol 4 with 1 and 2.

Se Reagent	Solvent	Reaction Conditions[a]	5 %	6 %
1	THF	3h, 50°C	71	20
	CH_2Cl_2	20h, r.t.	45	30
	THF	4Å, 20h, r.t.	73	8
	C_6H_6	4h, reflux	82	13
	pyridine	20h, r.t.	23	10
	CH_2Cl_2	P_2O_5, 3d, r.t.	18	74
	Ac_2O	1h, r.t.	72	0
2	THF	20h, r.t.	0	12
	THF	H_2O, 48h, r.t.	14	40
	CH_2Cl_2	2h, r.t.	6	77
	CH_2Cl_2	CSA[b], 3d, r.t.	9	69
	Ac_2O	1h, r.t.	70	0

a - r.t. is room temperature

b - CSA is camphorsulphonic acid

Oxidation of 3,5-di-tert-butylphenol 4 with the anhydride 1 led preferentially to the ortho-quinone 5, and with the acid 2 to the para-quinone 6. This trend is greatly improved by the solvent. Thus, THF and benzene are the best solvents for ortho-oxidation with 1, and methylene dichloride the best solvent for para-oxidation with 2. Although pyridineseleninic derivatives are better oxidants for olefins than the corresponding benzene derivative[7], oxidation of phenol 4 with 1 in pyridine was very slow. When the oxidation was performed in acetic anhydride, a fast reaction occurred to give only the ortho-quinone, whether with the anhydride 1 or the acid 2. Under these



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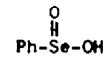

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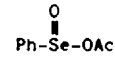

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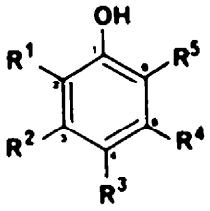
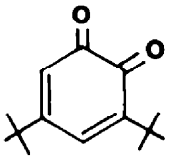
Phenolic compounds

Formula	R^1	R^2	R^3	R^4	R^5
4	H	t-Bu	H	t-Bu	H
8	t-Bu	H	t-Bu	H	H
9	Me	H	H	H	Me
15	t-Bu	H	H	H	t-Bu
17	i-Pr	H	H	Me	H
20	Me	H	H	i-Pr	H
21	t-Bu	H	t-Bu	H	t-Bu





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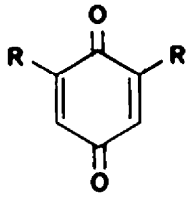
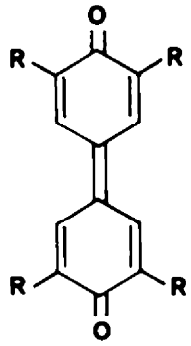
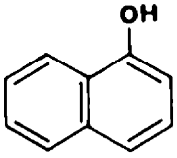


6 R = t-Bu
10 R = Me



14 R = Me
16 R = t-Bu



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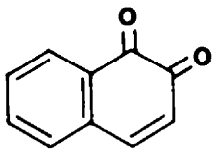

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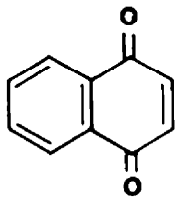

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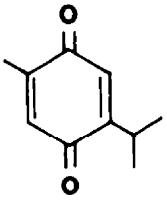

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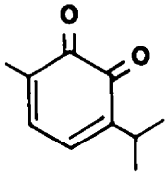

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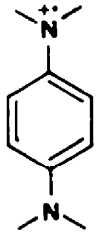

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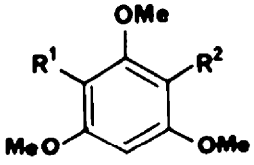
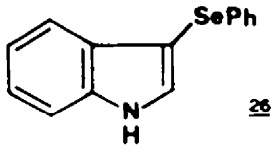


23 $R^1 = R^2 = H$
24 $R^1 = H$, R^2 = SePh
25 $R^1 = R^2$ = SePh



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conditions, the effective reagent must be a mixed anhydride such as 7. Water does not significantly affect the reactions with the seleninic acid 2, but the ortho-isomer is favoured under anhydrous conditions. Thus, benzeneseleninic anhydride 1 reacts with phenol 4 under anhydrous conditions in benzene or THF, preferably at 60-80°C, to give essentially the ortho-quinone. On the other hand, benzeneseleninic acid 2 reacts with 4 in methylene dichloride to give essentially the para-quinone.

Table 2 - Oxidation of Various Phenols with 1 and 2.

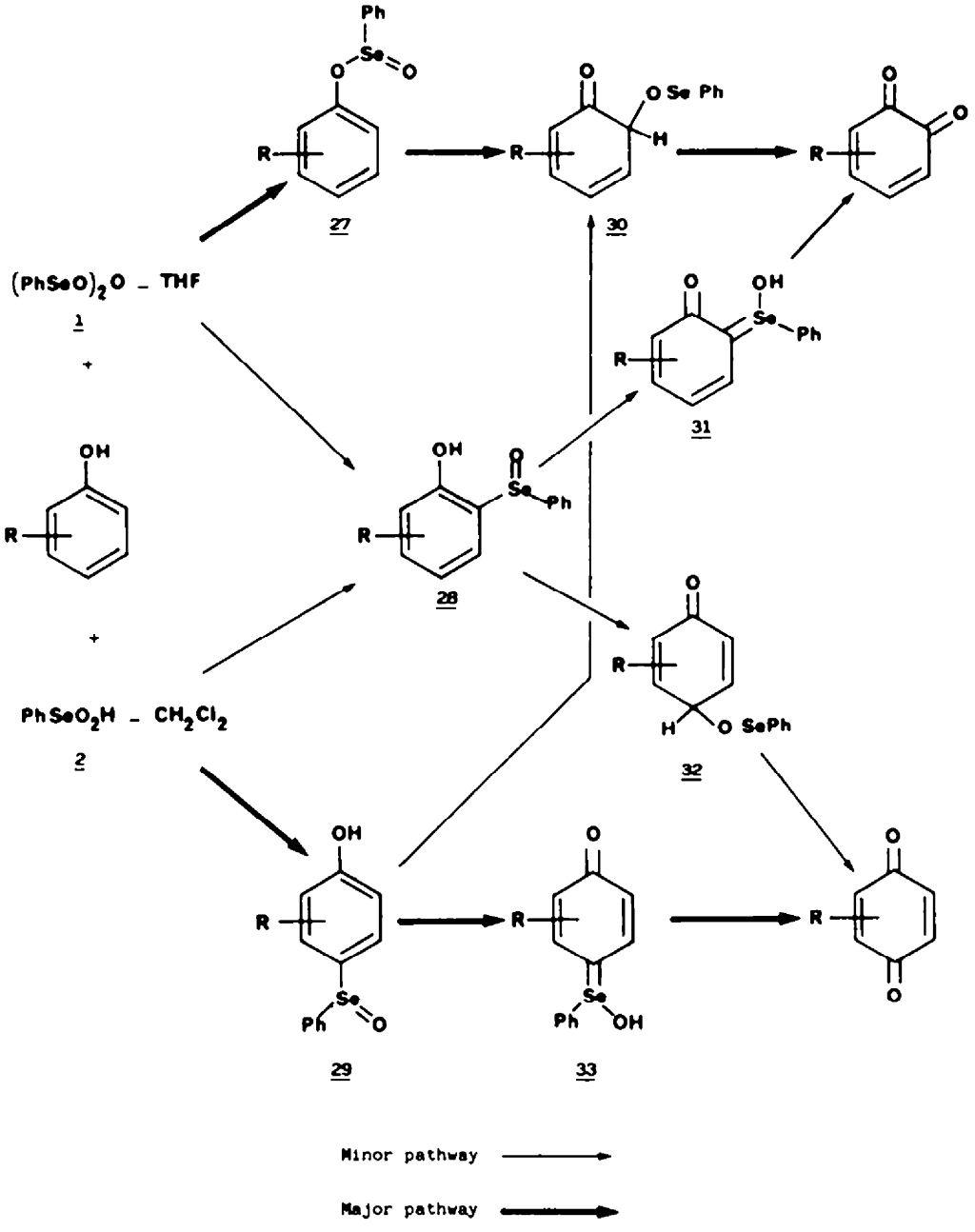
Phenol	Se Reagent	Reaction Conditions	Products (%)
8	2	CH_2Cl_2, 5h, r.t.	5 (42)
8	1	THF, 5h, r.t.	5 (68)[a]
9	2	CH_2Cl_2, 1h, reflux	10 (40)
9	1	DMF, 2h, r.t.	10 (25)[b]
11	1	THF, 2h, 50°C	12 (62), 13 (4)[c]
11	2	CH_2Cl_2, 18h, r.t.	12 (6), 13 (36)
15	1	THF, 1h, 50°C	6 (9), 16 (76)
15	2	CH_2Cl_2, 20h, r.t.	6 (11), 16 (77)
17	1	THF, 24h, 60°C	18 (27), 19 (58)
17	2	CH_2Cl_2, 2h, r.t.	18 (75), 19 (19)
20	1	THF, 24h, 60°C	18 (25), 19 (60)
20	2	CH_2Cl_2, 2h, r.t.	18 (82), 19 (7)

a : Ref. 18 ; b : Ref. 3 ; c : Ref. 16.

This selectivity pattern was further exemplified with other phenols (Table 2). In the case of 2,6-dimethylphenol 9, oxidation with the anhydride 1 led to various products. Oxidation of the sodium anion of 9 in THF afforded only the ortho-hydroxydienone, isolated as its dimer. But oxidation of the phenol 9 with 1 in DMF led to a mixture of the hydroxydienone (5%), the para-quinone 10 (25%) and the diphenoquinone 14 (40%)[3]. As expected, oxidation of 9 with the acid 2 led to a higher yield of 10 (40%). When the 2,6-di-tert-butyl analogue 15 was treated under these conditions, only a small amount of the para-quinone 6 was isolated from the oxidations with 1 or 2, the major product being the diphenoquinone 16. The radical mechanism of this reaction was supported by the e.s.r. observation of the aryloxyl radical of 2,4,6-tri-tert-butylphenol 21 when treated with 1 in THF (g 2.0051±0.0004 ; a_{Hm} 1.76±0.05G) or with 2 in CH_2Cl_2 (g 2.0049±0.0004 ; a_{Hm} 1.89±0.05G). Similarly the Würster radical cation 22 was observed in the reaction of N,N,N',N'-tetramethyl-p-phenylenediamine with 1 in THF (g 2.0037±0.0004 ; $a_{H(CH3)}$ 1.77±0.05G ; $a_{H(CH)}$ 6.80±0.05G ; a_N 6.93±0.05G) or with 2 in CH_2Cl_2 (g 2.0034±0.0004 ; $a_{H(CH3)}$ 1.77±0.05G ; $a_{H(CH)}$ 6.82±0.05G ; a_N 6.99±0.05G).

In the oxidation of some phenols, phenylselenylated derivatives have been observed, resulting from the trapping of intermediately formed phenylselenium (II) species by the phenolic substrate itself. We considered that such by-products could be eliminated through addition of a more nucleophilic non-oxidizable trapping agent. Such a reaction seemed possible when 1,3,5-trimethoxybenzene 23 was used as an internal standard for NMR monitoring of the oxidation of thymol and carvacrol. The mono- and di-phenylseleno derivatives 24 and 25 were formed. Oxidation of phenols prone to phenylselenylation with 1 or 2 in the presence of 1,3,5-trimethoxybenzene led

nevertheless to complex mixtures from which only the phenylseleno compounds 24 or 25 were recovered. Other trapping agents were also used, and indole proved to be the most efficient. Thus, 3-phenylselenoindole 26 was the only selenium containing product obtained in the oxidation of indoline by 1[8], in the presence of 23. When α-naphthol 11 was oxidized by 1 in the presence of indole, a good yield of the ortho-quinone and of the phenylseleno compound 26 was obtained. Apart

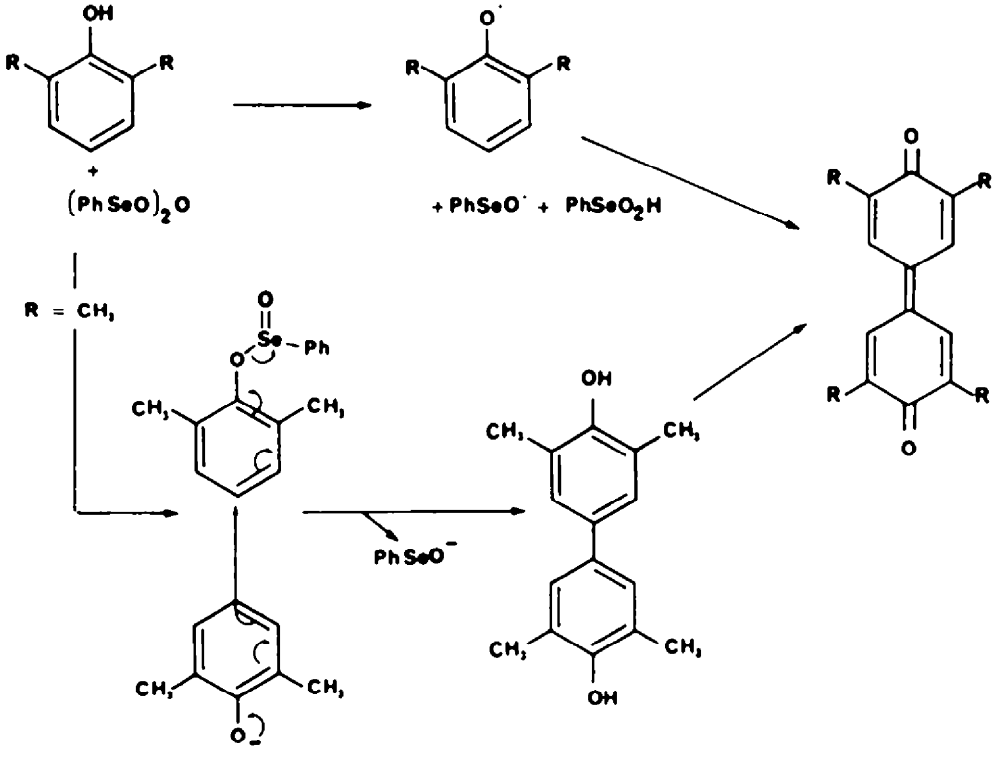


Scheme 2 - Mechanisms of Phenol Oxidation by Benzeneseleninic Derivatives 1 and 2.

from a trace amount of diphenyldiselenide, no other selenium containing derivative was detected.

Various mechanisms have been postulated to rationalize the product distribution and the ortho selectivity leading to ortho-quinones or α-hydroxycyclohexadienones, depending upon the α-substitution. The study of the influence of various factors, such as the nature of the Se (IV) reagent, the solvent and the reaction conditions, leads to a better understanding of the various pathways (Scheme 2). Thus, under nucleophilic reaction conditions (THF or benzene, base, anhydride 1), the major pathway involves the formation of the O-seleninyl ester 27 of the phenol. Sigmatropic rearrangement leads to the ortho-hydroxylated derivatives 30. In the reaction of the acid 2 in acetic anhydride, the ortho selectivity implies the formation of a mixed anhydride such as 7, reacting with the phenol to give the O-seleninate. A minor pathway could result from ortho C-seleninylation of the phenol. This intermediate 28 can then undergo a seleno-Pummerer rearrangement to the ortho-quinone, or (in its ketonic form) a sigmatropic rearrangement to the para-hydroxylated derivatives 32. This minor pathway could therefore explain the formation of the para-quinone.

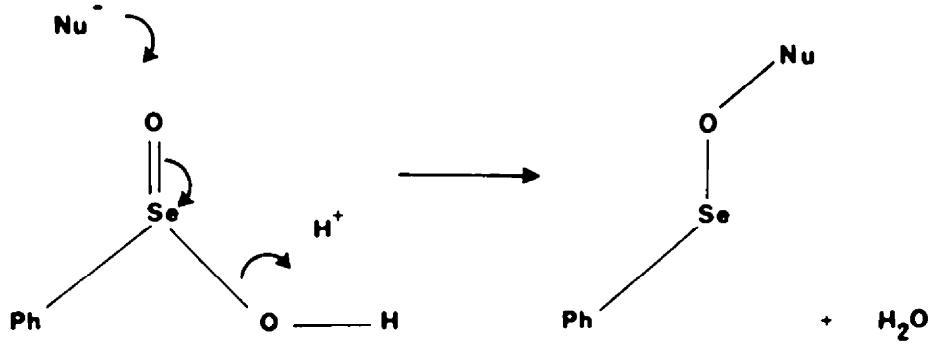
Under electrophilic reaction conditions (CH_2Cl_2, acid 2), formation of the arylphenylselenoxides 28 and 29 is now favoured. The ortho or para orientation is mostly guided by steric hindrance of the various substituents of the phenol. Again, these intermediates can undergo either of the two reductive fragmentation pathways : the sigmatropic rearrangement (29 → 30 or 28 → 32) or the seleno-Pummerer rearrangement (28 → 31 and 29 → 33).



Scheme 3 - Oxidation of 2,6-Disubstituted Phenols.

In the case of 2,6-disubstituted phenols, a radical pathway takes place as a minor (2,6-dimethylphenol) or unique (2,6-di-tert-butylphenol) route, leading to the corresponding diphenoquinones. Although an electron transfer between 1 and the phenol occurs with 2,4,6-tri-tert-butylphenol 21, a phenolate radical mechanism for the general case could not explain the selectivities of the oxidation reactions and the difference between the reagents 1 and 2 (Scheme 3).

In all the work on the oxidizing properties of benzeneseleninic anhydride that we carried out before[1,3] we always interpreted the reagent as mildly electrophilic in the sense $(PhSe{=}O)^{+}(PhSeO_2)^{-}$. There is no reason to change this analysis of the data. Benzeneseleninic acid might, however, be different. Thus (Scheme 4), polarisation in the sense shown, with water as a leaving group, could explain why the hindered 4-position in 4 is attacked so easily. Indeed, the analogue of 29 derived from 4 would be a very hindered compound. The direct formation of a derivative of type 32 (Scheme 2) would seem more likely. In that case the easy oxidation of phenol 4 would be explained for the 2-position by the mechanism 27→30 (Scheme 2), involving a first reaction with the unhindered phenolic hydroxyl and, for the 4-position, by the attack on the unhindered oxygen of the benzeneseleninic acid (Scheme 4).



Scheme 4

Be this as it may, the results now recorded show that for phenol oxidation the two reagents behave differently. The preferential ortho-oxidation by benzeneseleninic anhydride is confirmed and thus the original conception of a sigmatropic rearrangement is strengthened. The different behaviour of benzeneseleninic acid, however it is interpreted, also reinforces the original concept[3].

ACKNOWLEDGEMENTS : We thank Dr. C. Giannotti very much for his help with the e.s.r. experiments.

EXPERIMENTAL

M.p.s. were determined with a Kofler hot stage apparatus and are uncorrected. N.M.R. spectra were determined for solutions in deuterochloroform with TMS as internal standard on a Varian E-M. 360 apparatus. IR spectra were recorded on a Perkin-Elmer 297 spectrometer. U.V. spectra were recorded on a Perkin-Elmer Lambda 5 UV-Vis Spectrophotometer. Mass spectra were recorded with an AEI MS-9 instrument. E.s.r. spectra were recorded on Bruker ER-420 and ER-100D apparatus equipped with Bruker ER-400X-RL or TR-4012 cavities. Deaerated solutions of the samples were maintained under argon in a quartz tube. All solvents and reagents were purified and dried by standard techniques. Column chromatography under light pressure was performed using Merck Kieselgel 60 (230-400 mesh).

General Procedure for the Oxidation of Phenols with Benzeneseleninic Anhydride 1 and Benzeneseleninic Acid 2. A solution of the phenol (3 mM) in 5 ml of the appropriate anhydrous solvent was added dropwise over 15 minutes to a mixture of 1 (0.795 g, 2.2 mM) or 2 (0.832 g, 4.4 mM) in the anhydrous solvent (10 ml) under an atmosphere of argon. The mixture was stirred at the indicated temperature. The reaction was monitored by t.l.c. and stopped when no evolution was noticed or when the substrate had disappeared. Ether or methylene dichloride (60 ml) was added and the organic phase was washed with saturated aqueous $NaHCO_3$ solution followed by water. The organic phase was dried (Na_2SO_4), the solvent distilled off and the residue purified by column chromatography.

Oxidation of 3,5-Di-tert- butylphenol 4. The oxidation reactions were performed on 4 (0.62 g) and column chromatography (eluant : hexane-methylene dichloride 1:1, followed by methylene dichloride) afforded diphenyldiselenide 3, 2,6-di-tert-butyl-1,4-benzoquinone 6, m.p. 64-67°C, lit.[9] 65-66°C and 3,5-di-tert-butyl-1,2-benzoquinone 5, m.p. 111-114°C, lit.[10] 114°C. *I - With benzeneseleninic anhydride 1* : a) 1 and 4 in THF gave, after 3 hrs at 50°C, 3 (0.526 g, 84%), 6 (0.155 g, 20%), and 5 (0.469 g, 71%). b) 1 and 4 in methylene dichloride gave, after 20 hrs at room temperature, 3 (0.464 g, 74%), 6 (0.199 g, 30%), and 5 (0.299 g, 45%). c) 1 and 4 in THF in the presence of molecular sieves (4A, 1 g) gave, after 20 hrs at room temperature, 3 (0.505 g, 81%), 6 (0.053 g, 8%), and 5 (0.485 g, 73%). d) 1 and 4 in benzene gave, after 4 hrs under reflux with azeotropic distillation, 3 (0.587 g, 94%), 6 (0.087 g, 13%), and 5 (0.540 g, 82%). e) 1 and 4 in pyridine gave, after 20 hrs at room temperature, 3 (0.174 g, 28%), 6 (0.071 g, 10%), and 5 (0.153 g, 23%). f) 1 and 4 in methylene dichloride in the presence of phosphorus pentoxide (5 g, 35 mM) gave, after 3 days at room temperature, 3 (0.526 g, 84%), 6 (0.490 g, 74%), and 5 (0.120 g, 18%). g) 1 and 4 in acetic anhydride gave, after 1 hr at room temperature, 3 (0.428 g, 68%) and 5 (0.475 g, 72%). *II - With benzeneseleninic acid 2* : a) 2 and 4 in THF gave, after 20 hrs at room temperature, 3 (0.126 g, 19%) and 6 (0.08 g, 12%). b) 2 and 4 in THF in the presence of water (1 ml) gave, after 48 hrs at room temperature, 3 (0.389 g, 62%), 6 (0.266 g, 40%), and 5 (0.09 g, 14%). c) 2 and 4 in methylene dichloride gave, after 2 hrs at room temperature, 3 (0.52 g, 83%), 6 (0.51 g, 77%), and 5 (0.04 g, 6%). d) 2 and 4 in methylene dichloride in the presence of camphorsulphonic acid (0.35 g, 1.5 mM) gave, after 3 days at room temperature, 3 (0.534 g, 85%), 6 (0.457 g, 69%), and 5 (0.058 g, 9%). e) 2 and 4 in acetic anhydride gave, after 1 hr at room temperature, 3 (0.415 g, 66%), 6 (traces) and 5 (0.465 g, 70%).

Oxidation of Phenols 8, 9, 11, 15, 17 and 20. - i) 2,4-Di-tert-butylphenol 8. Reaction of 8 (0.62 g) with 2 in methylene dichloride gave, after 5 hrs at room temperature, 3 (0.579 g, 93%) and 5 (0.278 g, 42%).

ii) 2,6-Dimethylphenol 9. Reaction of 9 (0.366 g) with 2 in methylene dichloride gave, after 1 hr at reflux and chromatography (eluant : methylene dichloride-hexane gradient), 3 (0.441 g, 70%) and 2,6-dimethyl-1,4-benzoquinone 10 (0.164 g, 40%), m.p. 68-71°C (EtOH), lit.[11] 72-73°C.

iii) 1-Naphthol 11. Reaction of 11 (0.442 g) with 2 in methylene dichloride gave, after 18 hrs at room temperature and chromatography (eluant : hexane-ether 4:1), 3 (0.399 g, 64%), 1,4-naphthoquinone 13 (0.172 g, 36%), m.p. 120-122°C, lit.[12] 125°C, and 1,2-naphthoquinone 12 (0.03 g, 6%), m.p. 145-146°C, lit.[13] 146-147°C.

iv) 2,6-Di-tert-butylphenol 15. a) Reaction of 15 (0.62 g) and 1 in THF gave, after 1 hr at 50°C and chromatography (eluant : hexane-ether 9:1), 3 (0.45 g, 72%), 16 (0.468 g, 76%), m.p. 246-247°C, lit.[14] 246°C, and 6 (0.072 g, 11%). b) Reaction of 15 with 2 in methylene dichloride gave, after 20 hrs at room temperature, 3 (0.44 g, 71%), 16 (0.474 g, 77%), and 6 (0.072 g, 11%).

v) Thymol 17. a) Reaction of 17 (0.45 g) and 1 in THF gave, after 24 hrs at 60°C and chromatography (eluant : hexane-ether gradient), 3 (0.57g, 93%), thymoquinone 18 (0.135 g, 27%), m.p. 40-45°C, lit.[15] 44-45°C, and 3-methyl-6-(2-propyl)-1,2-benzoquinone 19 (0.286 g, 58%), m.p. 58-61°C, lit.[16] 60-61°C. b) Reaction of 17 with 2 in methylene dichloride gave, after 2 hrs at room temperature, 3 (0.495 g, 79%), 18 (0.371 g, 75%), and 19 (0.094 g, 19%).

vi) Carvacrol 20. a) Reaction of 20 (0.45 g) and 1 in THF gave, after 24 hrs at 60°C, 3 (0.551 g, 88%), 18 (0.124 g, 25%), and 19 (0.295 g, 60%). b) Reaction of 20 with 2 in methylene dichloride gave, after 2 hrs at room temperature, 3 (0.529 g, 85%), 18 (0.405 g, 82%), and 19 (0.035 g, 7%).

Oxidation of 4-tert-butylphenol in the presence of 1,3,5-trimethoxybenzene 23. a) The reaction of 4-tert-butylphenol (0.45 g), 1 (1.08 g), and 23 (0.084 g) in THF (15ml) gave, after 24 hrs at room temperature and chromatography (eluant : hexane-ether gradient), 1,3-diphenylseleno-2,4,6-trimethoxybenzene 25 (0.190 g, 79%) m.p. 126-128°C (CH_2Cl_2-EtOH), ν_{max} ($CHCl_3$) 1565,1340, and 1100cm^{-1} ; δ (C_6D_6) 6.80-6.10 (10H,m,C_6H_5Se), 5.2 (1H,s,ArH), 3.0 (3H,s,CH_3O), and 2.5 (6H,s,CH_3O) ; $_{max}$ (EtOH) 257 (22600) and 224 (32700)nm ; m/z 479 (M^+,100) and 242 (45) (Found : C, 52.53 ; H, 4.15 ; O, 10.21. $C_{21}H_{20}O_3Se_2$ requires C,52.73 ; H, 4.21 ; O, 10.03%). b) When the above reaction was performed with 23 (0.505 g), 24 was isolated (0.785 g, 80%), m.p. 105-107°C (CH_2Cl_2, EtOH) ; ν_{max} ($CHCl_3$) 1565 and 1100cm^{-1} ; δ (C_6D_6) 6.8-6.1 (5H,m,C_6H_5Se), 5.3 (2H,s,ArH), 2.5 (3H,s,CH_3O), and 2.4 (6H,s,CH_3O) ; m/z 307 (M^+-CH_3,30), 242(65), 91(75), and 77(100). (Found : C, 55.67 ; H, 5.05 ; O, 15.03. $C_{15}H_{16}O_3Se$ requires C, 55.73 ; H, 4.99 ; O, 14.85%).

Oxidation of Indoline in the Presence of 23. The reaction of indoline (0.225 ml) with 1 (0.36 g) and 23 (0.675 g) in THF (5ml) gave, after 2 hrs at room temperature and chromatography (hexane-CH_2Cl_2 3:2 followed by CH_2Cl_2), 23 (0.620 g, 92%) and 3-phenylselenoindole (0.48 g, 88%), m.p. 140-142°C, lit.[8] 143°C.

Oxidation of 1-Naphtol 11 in the Presence of Indole. A mixture of 11 (0.144 g), 1 (0.240 g) and indole (0.118 g) in benzene (10 ml) was stirred under reflux for 1 hr under an atmosphere of argon. Ortho-phenylene diamine (0.108 g) was added and the mixture stirred under reflux for 2 hrs. Fractional crystallization afforded 1,2-benzophenazine (0.148 g, 64%) m.p. 142-144°C (C_6H_6), lit.[17] 142°C and 26 (0.227g, 81%).

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