Persistent Nitrogen-centered Free Radicals, *N*-(Arylthio)-3,5-di-*t*-butylphenylaminyls. The Reactions with Phenols[1)]

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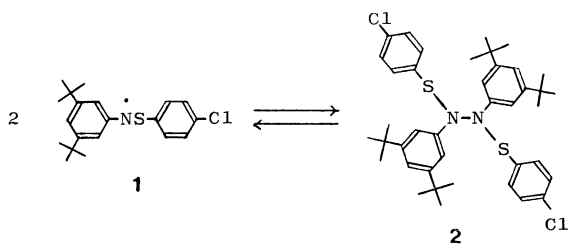
The reactions of *N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylaminyl (**1**) with phenols were examined. The reaction with 2,6-dimethyl- and di-*t*-butylphenols gave 2,6-dimethyl- and di-*t*-butyl-*p*-benzoquinone 3,5-di-*t*-butylphenylimines, respectively, in excellent yields. In the reaction with unsubstituted phenol, 2,6-bis[*N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylamino]-*p*-benzoquinone 3,5-di-*t*-butylphenylimine was obtained in 32—56% yields. On the other hand, the reactions with *p*-substituted phenols such as *p*-cresol, *p*-*t*-butylphenol, and 2,4-di-*t*-butylphenol, gave phenols which were substituted by **1** at the *ortho*-positions to the OH group. Furthermore, the reactions with *o*-cresol, 2,6-di-*t*-butyl-*p*-cresol, and 1-naphthol were examined. On the basis of these results, plausible mechanisms for the reactions are presented.

Reactions of phenols with nitroxide radicals have been widely studied from the synthetic viewpoint. For example, the reaction of potassium nitrosodisulfonate (Fremy's salt) with phenols, well-known as the Teuber reaction,[2)] gave a variety of quinones, usually in excellent yields. Similarly, the reactions using organic nitroxides afforded quinones in relatively good yields.[3,4)]

In contrast to the widely studied reactions of nitroxide radicals with phenols, the reactions with nitrogencentered free radicals have rarely been investigated. Rieker *et al.* reported that phenylamino radicals reacted with phenols to give quinone imines in 5—40% yields.[5)] On the other hand, the reactions reported by Barton *et al.* of bis(arylthio)aminyl radical with phenols gave quinone *N*-thioimines in fair to good yields.[6)]

In a continuous study on *N*-thioaminyl radicals ($R_1\dot{N}SR_2$),[1)] we have found that *N*-(arylthio)-3,5-di-*t*-butylphenylaminyls persist in solution, even in the presence of oxygen and can be isolated as crystalline dimers which dissociate, upon dissolution, into the original radicals with relatively large equilibrium constants.[7)]

In order to examine the properties of this new class of nitrogen-centered free radicals, we carried out the reactions of *N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylaminyl (**1**) with a variety of phenols. In this paper we wish to report the results.



Results and Discussion

The reactions of **1** with phenols were carried out at room temperature under a nitrogen atmosphere. The completion of the reactions was indicated by discharge of the dark blue color attributable to **1**. The results of the reactions are summarized in Table 1.

Table 1. Results of the reactions of **1** with phenols[a)]

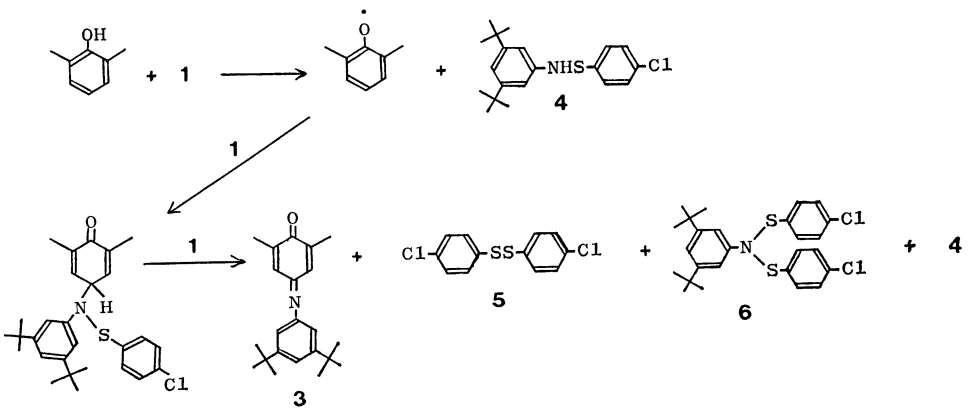
Phenol	Molar ratio of **1**/Phenol	Products (Yield/%)[b)]
2,6-Me_2	3.0	**3**(96)
2,6-*t*-Bu_2	3.0	**7**(92)
Unsubstituted	3.0	**11**(32)
Unsubstituted	5.4	**11**(56)
2-Me	1.0	**15**(13)
2-Me	3.0	**15**(57)
1-Naphthol	1.0	**17**(26), **18**(trace)
1-Naphthol	3.0	**17**(39), **18**(22)
4-Me	4.0	**19**(≧86)[c)]
4-*t*-Bu	1.0	**22**(22), **24**(9.8)
4-*t*-Bu	2.0	**22**(29), **24**(30)
4-*t*-Bu	3.8	**22**(trace), **24**(82)
2,4-*t*-Bu_2	2.0	**26**(90)
2,6-*t*-Bu_2-4-Me	2.0	**27**(61)

a) In benzene at room temperature. b) Iolated yields based on starting phenol. c) Based on the isolated yield (86%) of **21**.

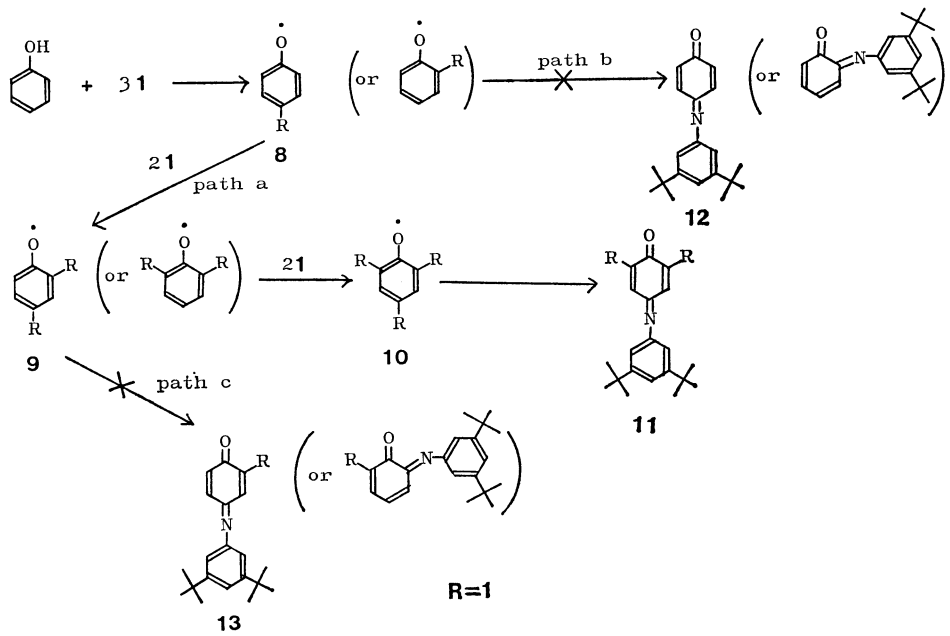
The reaction of 2,6-dimethylphenol with 3 equiv. (1.5 equiv. of **2**) of **1** was complete in 1 min on addition of the phenol, and the resulting orange-red reaction mixture gave 2,6-dimethyl-*p*-benzoquinone 3,5-di-*t*-butylphenylimine (**3**) almost quantitatively. The other products from the reaction were *N*-(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**4**), and small amounts of bis(p-chlorophenyl) disulfide (**5**) and *N*,*N*-bis(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**6**). Based on these products, this reaction mechanism can be reasonably described as in Scheme 1.

Similarly, 2,6-di-*t*-butylphenol reacted rapidly with 3 equiv. of **1** to give 2,6-di-*t*-butyl-*p*-benzoquinone 3,5-di-*t*-butylphenylimine (**7**) in 92%. This imine is probably produced by the same mechanism as above.

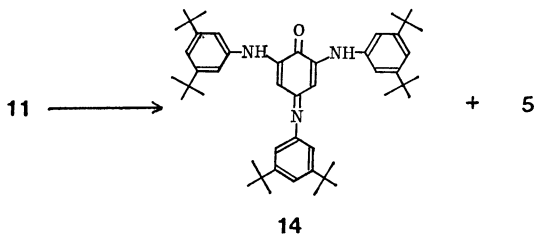
The reaction of unsubstituted phenol with 5.4 equiv. of **1** gave only **11** as quinone imine in 56% yield, and other quinone imines such as **12** and **13** were not found among the products. Quinone imine **11** was relatively unstable, being decomposed slowly in hydrocarbon solvents, and rapidly in methanol to **14** and bis(*p*-chlorophenyl) disulfide (Scheme 3). A plausible mechanism for the formation of **11** is represented



Scheme 1.



Scheme 2.



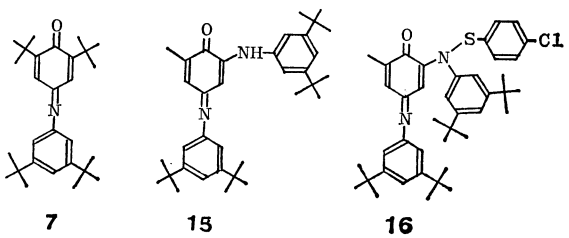
Scheme 3.

in Scheme 2. This reaction requires 7 equiv. of **1**, provided that the phenol is converted exclusively into **11**. However, even when the ratio of **1** to the phenol was 3, the quinone imine formed was only **11**. This interesting observation suggests that addition (path a) of **1** to the intermediate phenoxyl radicals **8** and **9**, giving **11** as the final product, is much faster than elimination (paths b and c) of a *p*-chlorophenylthiyl radical from the phenoxyl radicals, giving **12** and **13**.

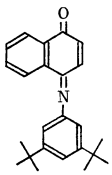
In the previously reported reactions of phenols with free radicals,[2-6] unsubstituted phenol was converted into the unsubstituted quinone or quinone imine, and monosubstituted phenols were usually converted into the monosubstituted quinones or quinone imines. Thus, the formation of the polysubstituted quinone imine such as **11** in the reaction with unsubstituted phenol is different from the previous results.

The reaction of *o*-cresol with 1—3 equiv. of **1** gave similarly only one quinone imine (**15**) in 13—57% yields. This quinone imine seems to be produced *via* **16**, by assumption of the above reaction.

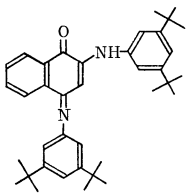
In contrast to the above reactions, the reactions of 1-naphthol with **1** gave two kinds of quinone imines (**17** and **18**). For example, a 1:3 equimolar mixture



of 1-naphthol and **1** afforded **17** and **18** in 39 and 22% yields, respectively. However, a 1:1 mixture of the naphthol and **1** gave only **17** in 26% yield (**18** was shown to be present in trace amounts by TLC inspection of the reaction mixture). In order to examine whether **18** was produced *via* **17** or not, a 1:2 equimolar mixture of **17** and **1** was stirred in benzene at room temperature for 2 h. TLC inspection showed no reaction occurred.

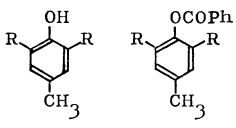


17



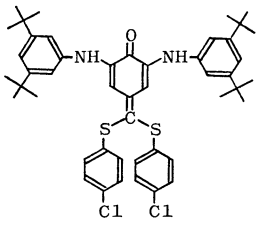
18

The reactions of **1** with *p*-substituted phenols such as *p*-cresol, *p*-*t*-butylphenol, and 2,4-di-*t*-butylphenol gave *ortho*-substituted phenols and no quinone imine was found among the products. For example, the reaction of *p*-cresol with 4 equiv. of **1** gave phenol **19** in good yield (≧86%). This phenol was not stable enough to be isolated. In order to confirm its structure, **19** was converted into a thermally stable benzoic ester **20** by treatment with benzoyl chloride. The phenol was decomposed slowly in benzene solution at room temperature (1 d for complete decomposition), and rapidly on reflux (30 min) to give dark yellow-blue crystals of **21** in 27% yield. The structure of this unexpected product was confirmed by IR, and ^{1}H and ^{13}C NMR spectroscopy, and the molecular weight (determined by vapor pressure osmometry).[5] The IR spectrum showed absorptions of NH at 3350 cm^{-1} and C=O at 1620 cm^{-1}, and in the ^{13}C NMR spectrum eight singlet peaks due to the aromatic, quinonoid, and carbonyl carbons and five doublet peaks due to the aromatic and quinonoid carbons were found. The observed molecular weight (807) was in good agreement with that calculated (798). Furthermore, the ^{1}H NMR spectrum and elemental analysis gave satisfactory results. On the basis of these instrumental analyses, we identified the crystal as **21**.



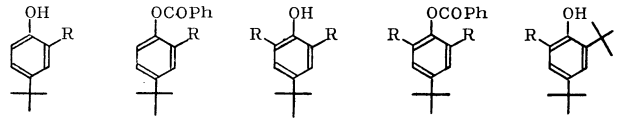
19 **20**

R=1



21

In the case of 4-*t*-butylphenol, 1:1 and 1:2 equimolar mixtures of the phenol and **1** gave two kinds of phenols, **22** and **24**, in 22—29 and 9.8—30%, respectively. However, a 1 3.8 equimolar mixture of the phenol and **1** afforded only **24** in 82% yield. On the other hand, the reaction of 2,4-di-*t*-butylphenol with 2 equiv. of **1** gave phenol **26** in 90% yield. These phenols, as well as **19**, were very unstable and could not be obtained as pure crystals. To confirm their structures, **22** and **24** were converted into the benzoic esters **23** and **25** by the same procedure as for **19**. In the case of **26**, however, the corresponding benzoic ester could not be obtained in the same manner, probably because of steric hindrance due to the bulky *o*-*t*-butyl group in **26**.



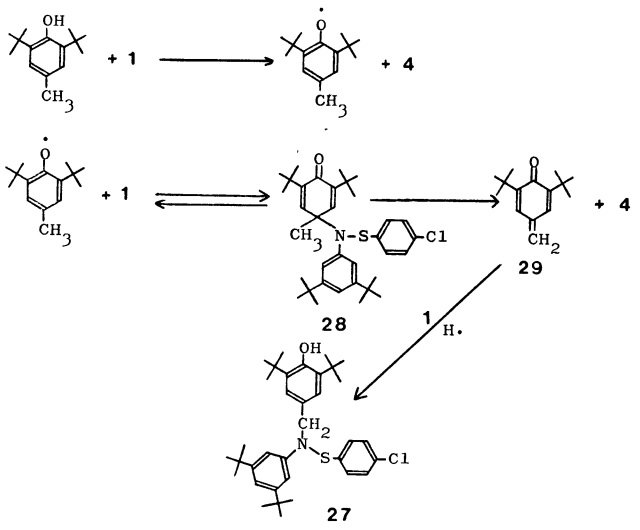
22 **23** **24** **25** **26**

R=1

The previously reported reactions of *p*-substituted phenols with nitroxide or bis(phenylthio)aminyl radicals gave *o*-quinones or *o*-quinone imines.[2-6] On the other hand, the reactions of **1** with *p*-substituted phenols afforded polysubstituted phenols such as **19** and **22**, but never *o*-quinone imines. This unusual result is worthy of note.

The reaction of 2,6-di-*t*-butyl-*p*-cresol with 2 equiv. of **1** yielded **27** in 61% yield. However, the careful TLC inspection of the reaction mixture revealed that **27** was not the product formed at the completion of the reaction. When the reaction mixture, which was light blue at the completion of the reaction, was allowed to stand at room temperature for 1 d, the color of the reaction mixture changed from light blue to light orange; TLC inspection revealed the complete decomposition of the initially formed product and the appearance of **27**. It seems that the initially formed product is **28**, which is a coupling product of **1** and 2,6-di-*t*-butyl-*p*-methylphenoxyl radical, and that **27** was produced through the coupling of **1** and quinone methide **29**. A similar reaction occured between 2,4,6-trimethylphenol and benzoyl *t*-butyl nitroxide radical.[4] An attempt to isolate **28** was unsuccessful.

Finally, the reaction of **1** with 2,4,6-tri-*t*-butylphenol



28 **29** **27**

Scheme 4.

was examined. However, the mixture of **1** and the phenol gave no coupling product.

Experimental

All melting points were taken on a Yanaco micro melting-point apparatus and are uncorrected. IR spectra were run on a JASCO Model IR-G spectrometer, and UV and visible spectra were recorded with a Hitachi 220 spectrophotometer. Mass spectra were taken with a Hitachi M-52 spectrometer. ^{1}H NMR spectra were recorded with a Hitachi Perkin Elmer R-20 (60 MHz) or JEOL PS-100 (100 MHz) spectrometer with tetramethylsilane as internal standard, and ^{13}C NMR spectra were taken on a JEOL FX-100 (25 MHz) spectrometer.

The phenols were commercially available and were purified by distillation or recrystallization from the appropriate solvents. Dimer **2** was prepared by our previous method.[7]

*General Procedure for the Reactions of **2** with Phenols.* Dimer **2** in benzene (30 ml) was stirred at room temperature until the dimer was completely dissolved in the solution (*ca.* 1 h). After nitrogen was bubbled through the stirred dimer solution for 30 min, a benzene solution (2 ml) of the phenol was added in one portion to the dimer solution, and the resulting reaction mixture was stirred for 10—120 min with continuous bubbling of nitrogen. After the solvent was removed by either evaporation or freeze-drying, the residue was chromatographed on alumina (Merck Art 1097; column size 3×40 cm) or silica gel (Wako gel C-200; column size 3×40 cm) with the appropriate solvents. The results are shown in Table 1.

Reaction with 2,6-Dimethylphenol. To a benzene solution of **2** (400 mg, 0.577 mmol) a benzene solution of 2,6-dimethylphenol (47 mg, 0.39 mmol) was added and the resulting red reaction mixture was stirred for 10 min, evaporated, and the residue chromatographed on alumina. Elution with benzene–hexane (1:5) gave a mixture of bis(*p*-chlorophenyl) disulfide (**5**) and *N*,*N*-bis(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**6**); subsequent elution with benzene–hexane (1:2) gave *N*-(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**4**) (227 mg, 0.653 mmol) and 2,6-dimethyl-*p*-benzoquinone 3,5-di-*t*-butylphenylimine (**3**) (120 mg, 0.371 mmol). The quinone imine was recrystallized from methanol to give red needles; mp 118—120 °C; IR (KBr): 1640 cm^{-1} (C=O); UV and vis (hexane): 451 (ε 3600), 291 (16500), and 270 (19800) nm; MS (70 eV): *m/e* (rel intensity), 325 (M^++2, 29), 324 (M^++1, 32), 323 (M^+, 100), 309 (23), 308 (74), 252 (32), 91 (21), and 57 (64); ^{1}H NMR (CCl_4): δ=1.33 (s, *t*-Bu, 18H), 1.86 and 2.02 (d, *J*=1.6 Hz, *syn*- and *anti*-CH_3, 6H), and 6.42—7.02 (m, aromatic and quinonoid, 5H). Found: C, 81.40; H, 9.04; N, 4.38%. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33%.

The mixture of **5** and **6** was treated on a preparative silica-gel TLC (Merck, Art 7730; 20×20 cm, 30 g) with benzene–hexane (1:20) as eluant to give 33 mg (0.12 mmol) of **5** and 28 mg (0.057 mmol) of **6**. The products **4**, **5**, and **6** were identified by comparison (mps and IR spectra) with authentic samples.[7,9]

Reaction with 2,6-Di-t-butylphenol. To a benzene solution of **2** (350 mg, 0.505 mmol) a benzene solution of 2,6-di-*t*-butylphenol (69 mg, 0.33 mmol) was added. The resulting red reaction mixture was stirred for 10 min, evaporated, and the residue chromatographed on alumina with benzene–hexane (1:5) to give 125 mg (0.307 mmol) of **7** which was recrystallized from methanol to afford red prisms; mp 75—77 °C; IR (KBr): 1640 cm^{-1} (C=O); UV and vis (hexane): 445 (ε 4040), 295 (16800), and 272 (17200) nm; MS (70 eV): *m/e* (rel intensity), 409 (M^++2, 19), 408 (M^++1, 31), 407 (M^+, 100), 392 (18), and 57 (45); ^{1}H NMR (CCl_4): δ=1.19 and 1.32 (s, *syn*- and *anti*-*t*-Bu, 18H), 1.32 (s, *t*-Bu, 18H), and 6.54—7.09 (m, aromatic and quinonoid, 5H). Found: C, 82.30; H, 10.22; N, 3.51%. Calcd for $C_{28}H_{41}NO$: C, 82.50; H, 10.14; N, 3.44%.

Reaction with Phenol. To a benzene solution of **2** (400 mg, 0.577 mmol) a benzene solution of phenol (36 mg, 0.38 mmol) was added and the resulting red reaction mixture was stirred for 10 min. The solvent was removed by freeze-drying and the resultant red powdery residue was chromatographed on silica gel with benzene–hexane (3:1), using a column cooled by circulating ice-water. The fractions of the red zone were collected and concentrated to *ca.* 30 ml below 10 °C under reduced pressure. The residual solvent (benzene) was then removed by freeze-drying to give red powdery crystals of **11** (120 mg, 0.122 mmol) (TLC one spot). Since this product was thermally unstable, recrystallization was unsuccessful. The results of instrumental and elemental analyses for the powdery **11** are as follows: IR (KBr): 1660 cm^{-1} (C=O); ^{1}H NMR (CCl_4)[10]: δ=1.18 (s, *t*-Bu, 18H), 1.25 (s, *t*-Bu, 36H), and 6.52—7.15 (m, aromatic and quinonoid, 19H). Found: C, 73.57; H, 7.59; N, 3.86%. Calcd for $C_{60}H_{73}Cl_2N_3OS_2$: C, 72.99; H, 7.45; N, 4.26%.

Similarly, the reaction of 400 mg (0.577 mmol) of **2** with 20 mg (0.21 mmol) of phenol gave 118 mg (0.120 mmol) of **11**.

*Conversion of **11** into **14**.* Quinone imine **11** (95 mg, 0.096 mmol) in 20 ml of methanol was stirred for 20 min at room temperature. After complete removal of the solvent in vacuum, the residue was chromatographed on alumina (column size 3×20 cm) with benzene–hexane (1:1) as eluant, giving 23 mg (0.080 mmol, 83%) of bis(*p*-chlorophenyl) disulfide and 62 mg (0.088 mmol, 92%) of quinone imine **14**. This quinone imine was recrystallized from methanol to give dark red prisms; mp 133—136 °C; IR (KBr): 3370 (NH) and 1630 cm^{-1} (C=O); UV and vis (hexane): 495 ε 8300), 414 (7300), and 271 (36800) nm; MS (70 eV): *m/e* (rel intensity), 703 (M^++2, 27), 702 (M^++1, 55), 701 (M^+, 100), and 57 (50); ^{1}H NMR (CCl_4): δ=1.12 (s, *t*-Bu, 18H), 1.19 (s, *t*-Bu, 18H), 1.36 (s, *t*-Bu, 18H), 6.46—7.01 (m, aromatic and quinonoid, 11H), and 6.82 (s, NH, 2H, exchanged by D_2O). Found: C, 81.80; H, 9.73; N, 5.84%. Calcd for $C_{48}H_{67}N_3O$: C, 82.12; H, 9.62; N, 5.98%.

The bis(*p*-chlorophenyl) disulfide isolated was identified by its IR spectrum.

*Direct Preparation of **14**.* 1) A reaction mixture, obtained from 400 mg (0.577 mmol) of **2** and 36 mg (0.38 mmol) of phenol, was evaporated and the residue was dissolved in 20 ml of methanol. The solution was stirred for 20 min at room temperature and the solvent was completely removed in vacuum, the residue was chromatographed on alumina. Elution with benzene–hexane (1:2) gave bis(*p*-chlorophenyl) disulfide and **4**, and subsequent elution with benzene–hexane (2:1) gave 95 mg (0.14 mmol, 37%) of **14**. 2) The reaction mixture, obtained from 400 mg (0.577 mmol) of **2** and 36 mg (0.38 mmol) of phenol, was refluxed in benzene for 30 min and evaporated. The resulting residue was chromatographed on alumina in the same manner as described above to give 90 mg (0.13 mmol, 33%) of **14**.

Reaction with o-Cresol. To a benzene solution of **2** (400 mg, 0.577 mmol) was added a benzene solution of *o*-cresol (41 mg, 0.38 mmol) and the resulting red reaction mixture was stirred for 10 min. The mixture was evaporated and the residue chromatographed on alumina, using a column

cooled by circulating ice-water. Elution with benzene–hexane (1:1) gave bis(*p*-chlorophenyl) disulfide, **4**, and **6**, and subsequent elution with benzene–hexane (2:1) gave 112 mg (0.22 mmol) of **15**. This quinone imine was dissolved in a small amount (2 ml) of benzene, 10 ml of hexane was added to the solution and cooled to 5 °C, giving dark red needles (this quinone imine was immediately decomposed in methanol and slowly in benzene and hexane at reflux); mp 175—176 °C; IR (KBr): 3330 (NH) and 1640 cm^{-1} (C=O); UV and vis (hexane): 486 (ε 6050) and 275 (22600) nm; MS (70 eV): *m/e* (rel intensity), 514 (M^++2, 48), 513 (M^++1, 93), 512 (M^+, 100), 455 (15), and 57 (74); ^1H NMR (CCl_4)[11]: δ=1.10, 1.18, 1.32, and 1.34 (s, *t*-Bu, 36H), 1.96 and 2.08 (d, J=1.4 Hz, *syn*- and *anti*-CH_3, 3H), and 6.24—6.88 (m, aromatic, quinonoid, and NH, 9H). Found: C, 81.59; H, 9.84; N, 5.15%. Calcd for $C_{35}H_{48}N_2O$: C, 81.98; H, 9.44; N, 5.46%.

Similarly, the reaction of 130 mg (0.188 mmol) of **2** with 41 mg (0.38 mmol) of *o*-cresol gave 26 mg (0.051 mmol) of **15**.

Reaction with 1-Naphthol. To a benzene solution of **2** (409 mg, 0.590 mmol) a benzene solution of 1-naphthol (56 mg, 0.39 mmol) was added. The resulting red reaction mixture was stirred for 120 min, evaporated, and the residue chromatographed on alumina with benzene–hexane (2:3). The fractions of the red zone (mixture of quinone imines **17** and **18**) were collected, concentrated, and the residue was run on a preparative alumina TLC (Merck, Art 1064; 20×40 cm, 80 g) to afford 52 mg (0.15 mmol) of **17** and 46 mg (0.084 mmol) of **18**. The quinone imines were recrystallized from methanol; **17**: red prisms; mp 148—150 °C; IR (KBr): 1650 cm^{-1} (C=O); UV and vis (hexane): 454 (ε 3460), 435 (sh, 3120), and 255 (22000) nm; MS (70 eV): *m/e* (rel intensity), 346 (M^++1, 47), 345 (M^+, 100), 330 (35), 274 (22), 140 (21), and 57 (52); ^1H NMR (CCl_4): δ=1.37 (s, *t*-Bu, 18H) and 6.56—8.52 (m, aromatic and quinonoid, 9H). Found: C, 83.03; H, 7.97; N, 4.02%. Calcd for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05%.

Quinone imine **18**: red prisms; mp 200—202 °C; IR (KBr): 3350 (NH) and 1650 cm^{-1} (C=O); UV and vis (hexane): 468 (ε 6770), 277 (25500), 248 (sh, 21000), and 235 (sh, 23200) nm; MS (70 eV): *m/e* (rel intensity), 550 (M^++2, 20), 549(M^++1, 57), 548 (M^+, 100), and 57 (28); ^1H NMR (CCl_4): δ=1.17 (s, *t*-Bu, 18H), 1.24 (s, *t*-Bu, 18H), 7.26 (s, NH, 1H, exchanged by D_2O), and 6.56—8.60 (m, aromatic and quinonoid, 11H). Found: C, 82.85; H, 8.96; N, 5.33%. Calcd for $C_{38}H_{48}N_2O$: C, 83.16; H, 8.82; N, 5.11%.

On the other hand, the reaction of 136 mg (0.196 mmol) of **2** with 56 mg (0.39 mmol) of 1-naphthol gave only 35 mg (0.10 mmol) of **17** (**18**: trace amounts from TLC inspection of the reaction mixture).

Reaction with p-*Cresol.* To a benzene solution of **2** (400 mg, 0.577 mmol) a benzene solution of *p*-cresol (31 mg, 0.29 mmol) was added and the resulting mixture stirred for 15 min, turning light greenish yellow. After the solvent was removed by freeze-drying, the residue was dissolved in 20 ml of dry benzene and cooled to 5 °C in an ice-water bath. To the solution was added 0.58 g (5.7 mmol) of triethylamine and 0.48 g (3.4 mmol) of benzoyl chloride with stirring, and the mixture was stirred for 20 min at 5 °C and for 3 h at room temperature. The mixture was washed with K_2CO_3 aq solution, then with water, and dried over anhyd $MgSO_4$. After filtration and concentration, the residue was chromatographed on alumina (Merck, Art 1097) with benzene–hexane (1:2) to give 218 mg (0.250 mmol, 86%) of **20**, which was recrystallized from methanol–benzene; colorless prisms; mp 167—168.5 °C; IR (KBr): 1745 cm^{-1} (C=O); ^1H NMR (CCl_4): δ=1.12 (s, *t*-Bu, 36H), 2.29 (s, CH_3, 3H), and 6.76—7.25 (m, aromatic, 21H). Found: C, 74.15; H, 6.70; N, 3.05%. Calcd for $C_{54}H_{60}Cl_2N_2O_2S_2$: C, 74.37; H, 6.94; N, 3.21%.

The reaction mixture, obtained from 400 mg (0.577 mmol) of **2** and 31 mg (0.29 mmol) of *p*-cresol, was refluxed for 30 min, turning dark red. After the mixture was evaporated, the residue was chromatographed on alumina. Elution with benzene–hexane (2:3) gave a mixture of **4** and **5**. Subsequent elution with benzene gave 63 mg (0.079 mmol, 27%) of **21**, which was recrystallized from methanol; dark yellow-blue needles; mp 138—140 °C; IR (KBr): 3350 (NH) and 1620 cm^{-1}; ^1H NMR (CCl_4): δ=1.29 (s, *t*-Bu, 36H) and 6.91—7.68 (m, aromatic, quinonoid, and NH, 18H). ^{13}C NMR ($CDCl_3$): δ=177.5 (s), 152.2 (s), 139.7 (s), 138.9 (s), 138.7 (s), 136.0 (s), 134.0 (s), 132.9 (d), 132.7 (s), 129.0 (d), 117.0 (d), 114.6 (d), 103.2 (d), 35.2 (s), and 31.6 (q); molecular weight determined by vapor pressure osmometry (Knauer; benzene, 45 °C): 807 (calcd: 798). Found: C, 70.46; H, 6.94; N, 3.38%. Calcd for $C_{47}H_{54}Cl_2OS_2$: C, 70.74; H, 6.82; N, 3.51%.

Reaction with p-t-*Butylphenol.* To a benzene solution of **2** (400 mg, 0.577 mmol) a benzene solution of *p-t*-butylphenol (87 mg, 0.58 mmol) was added and the reaction mixture stirred for 30 min, turning colorless or wine-red. The solvent was removed by freeze-drying and the residue was chromatographed on silica gel, using a column cooled by circulating ice-water. Elution with benzene–hexane (2:3) gave 177 mg (0.509 mmol) of **4** and 145 mg (0.172 mmol) of **24**, and subsequent elution with benzene–hexane (2:1) gave 84 mg (0.17 mmol) of **22**. Isolation of **22** and **24** was performed by the same procedure as for **11**. Since these isolated phenols contained small amounts of impurities, they were recrystallized. However, this caused further decomposition of the phenols. In order to confirm their structures, the phenols were converted into stable benzoic esters **23** and **25** by treating them with benzoyl chloride. Phenol **22**: IR (KBr): 3420 cm^{-1} (OH); ^1H NMR (benzene-d_6): δ=1.07 (s, *t*-Bu, 9H), 1.23 (s, *t*-Bu, 18H), 5.06 (s, OH, 1H), and 6.70—7.28 (m, aromatic, 10H).

Phenol **24**: IR (KBr): 3480 cm^{-1} (OH); ^1H NMR (benzene-d_6): δ=1.00 (s, *t*-Bu, 9H), 1.26 (s, *t*-Bu, 36H), 5.36 (s, OH, 1H), and 6.77—7.30 (m, aromatic, 16H).

The reaction of 400 mg (0.577 mmol) of **2** with 175 mg (1.17 mmol) of *p-t*-butylphenol gave 126 mg (0.254 mmol) of **22** and 96 mg (0.11 mmol) of **24**. On the other hand, the reaction of 400 mg (0.577 mmol) of **2** with 46 mg (0.31 mmol) of the phenol gave only 211 mg (0.251 mmol) of **24** (**22**: trace amounts from TLC inspection).

*Conversion of **22** into Benzoic Ester **23**.* To a stirred solution of **22** (142 mg, 0.286 mmol) and triethylamine (0.58 g, 5.7 mmol) in dry benzene (10 ml), 0.24 g (1.7 mmol) of benzoyl chloride was added at 5 °C. After being stirred for 2 h at room temperature, the reaction mixture was passed through a short column (4×10 cm) packed with alumina (Merck, Art 1097; eluant benzene) to remove unreacted benzoyl chloride. After concentration of the eluate, methanol–water was added to the residue to give 168 mg (0.280 mmol, 98%) of a light yellow powder (TLC one spot), which was recrystallized from methanol–water: colorless prisms; mp 134—136 °C; 141 mg (0.235 mmol, 82%); IR (KBr): 1745 cm^{-1} (C=O); ^1H NMR (CCl_4): δ=1.15 (s, *t*-Bu, 18H), 1.32 (s, *t*-Bu, 9H), and 6.78—7.68 (m, aromatic, 15H). Found: C, 73.72; H, 6.94; N, 2.28%. Calcd for $C_{37}H_{42}ClNO_2S$: C, 74.04; H, 7.05; N, 2.33%.

*Conversion of **24** into Benzoic Ester **25**.* The conversion

was carried out by the same procedure as that for **22**. To a stirred solution of **24**(125 mg, 0.148 mmol) and triethylamine (0.58 g, 5.7 mmol) in dry benzene (10 ml) was added 0.24 g (1.7 mmol) of benzoyl chloride at 5 °C. The reaction mixture was stirred for 2 h at room temperature and passed through a short column packed with alumina. After concentration of the eluate, methanol–water was added to the residue to give 132 mg (0.140 mmol, 95%) of colorless crystals (TLC one spot), which were recrystallized from methanol–benzene: colorless needles; mp 176—177 °C; 111 mg (0.117 mmol, 79%); IR (KBr): 1750 cm^{-1} (C=O); ^1H NMR (CCl_4): δ=1.16 (s, *t*-Bu, 36H), 1.24 (s, *t*-Bu, 9H), and 6.79—7.35 (m, aromatic, 21H). Found: C, 72.36; H, 7.01; N, 2.85%. Calcd for $C_{57}H_{66}Cl_2N_2O_2S_2$: C, 72.36; H, 7.03; N, 2.96%.

Reaction with 2,4-Di-t-butylphenol. To a benzene solution of **2** (200 mg, 0.289 mmol) a benzene solution of 2,4-di-*t*-butylphenol (60 mg, 0.29 mmol) was added and the resulting reaction mixture was stirred for 20 min, turning colorless or wine-red. The solvent was removed by freeze-drying and the residue was chromatographed on silica gel, using a column cooled by circulating ice-water. Elution with benzene–hexane (1:3) gave 143 mg (0.259 mmol) of powdery **26**, which was isolated from the eluate by the same procedure as for **11**. Since the phenol isolated was contaminated with trace amounts of bis(*p*-chlorophenyl) disulfide, it was recrystallized. However, this resulted in further decomposition of the phenol. IR (KBr): 3500 cm^{-1} (OH); ^1H NMR (benzene-d_6): δ=1.14 (s, *t*-Bu, 9H), 1.24 (s, *t*-Bu, 18H), 1.53 (s, *t*-Bu, 9H), 5.53 (s, OH, 1H), and 6.70—7.35(m, aromatic, 9H).

Reaction with 2,6-Di-t-butyl-p-cresol. To a benzene solution of **2** (400 mg, 0.577 mmol) a benzene solution of 2,6-di-*t*-butyl-*p*-cresol (125 mg, 0.567 mmol) was added and the reaction mixture was stirred for 10 min, turning light blue. After standing for 1 d at room temperature, the resulting yellow reaction mixture was evaporated and the residue chromatographed on alumina with benzene–hexane (1:2) to give 196 mg (0.346 mmol) of **27** as a yellow oil, which was recrystallized from methanol–water (20:1): light orange prisms: mp 130—131 °C; IR (KBr): 3580 cm^{-1} (OH); MS (70 eV): *m/e* (rel intensity), 565 (M^+, 4), 422 (16), 346 (83), 219 (100), 204 (30), and 57 (44); ^1H NMR (CCl_4): δ= 1.22 (s, *t*-Bu, 18H), 1.35 (s, *t*-Bu, 18H), 4.73 (s, CH_2, 2H), 4.92 (s, OH, 1H), and 6.76—7.17 (m, aromatic, 9H). Found: C, 74.50; H, 8.51; N, 2.22%. Calcd for $C_{35}H_{48}ClNOS$: C, 74.24; H, 8.54; N, 2.47%.

References

1) Part 18 in the series "ESR Studies of Nitrogen-Centered Free Radicals." For Part 17, see: Y. Miura, A. Yamamoto, Y. Katsura, M. Kinoshita, S. Sato, and C. Tamura, *J. Org. Chem.*, **47**, 2618 (1982).

2) H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, **71**, 229 (1971).

3) A. R. Forrester and R. H. Thomson, *J. Chem. Soc., C*, **1966**, 1844.

4) S. A. Hussain, T. C. Jenkins, and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2809.

5) A. Rieker and H. Kessler, *Z. Naturforsch., B*, **21**, 939 (1966).

6) D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1031.

7) Y. Miura, A. Yamamoto, Y. Katsura, and M. Kinoshita, *J. Org. Chem.*, **45**, 3875 (1980).

8) The mass spectrum of **21** showed no peak, probably due to the decomposition of the compound to polymeric products.

9) Y. Miura, A. Yamamoto, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **54**, 3215 (1981).

10) Quinone imine **11** was gradually decomposed during the NMR measurement.

11) The ratio of *syn*:*anti* isomers is 1:5 (or 5:1) from the NMR spectrum.