of MNDO in this connection and because this reaction is of interest as one of the simplest pericyclic processes. While a number of calculations have been reported[17] for it, none of these has used MNDO.

Figure 4 indicates the geometries and heats of formation calculated here for **12**, **13**, and the transition state for their interconversion. No experimental values are available for comparison.

Figure 5 is an ORTEP plot of the transition state showing the transition coordinate, i.e., the eigenvector corresponding to the normal mode with a negative force constant.

The reaction takes place conrotatorily, as expected[18] and as predicted by all previous calculations.[17] Our values lead to a heat of reaction (−30 kcal/mol) which agrees very well with that (−31 kcal/mol) given by an ab initio calculation,[17] but our estimate of the activation energy (−18.6 kcal/mol) is considerably less than the ab initio value (27 kcal/mol). The ab initio value is, however, likely to be too high because the procedure used to locate the transition state was inadequate.[13]

Judging by these results, there seems no reason to believe that MNDO encounters any special problems in systems of this kind. Calculations[19] for a number of anions have indeed indicated that difficulties arise only for very small anions where most of the formal negative charge is concentrated on a single atom.

Acknowledgment. this work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008), the National Science Foundation (Grant CHE78-03213), and the Robert A. Welch Foundation (Grant F-126).

Registry No. **2**, 54078-18-1; **3**, 54078-26-1; **5**, 81389-28-8; **6**, 81389-29-9; **7**, 81389-30-2; **8**, 81389-31-3; **9**, 81389-32-4; **10**, 81389-33-5; **12**, 1724-45-4; **13**, 1724-46-5; **14**, 5281-20-9.

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[17] (a) Clark, D. T.; Armstrong, D. R. *Theor. Chim. Acta* **1969**, *14*, 370. (b) Clark, D. T.; Smale, G. *Tetrahedron Lett.* **1968**, 3673.

[18] (a) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761. (b) Dewar, M. J. S. *Tetrahedron Suppl.* **1966**, *8*, 75. (c) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 325.

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[(4-Nitrophenyl)thio](2,4,6-tri-*tert*-butylphenyl)aminyl: Its Preparation, Isolation, and Molecular Structure[1]

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[(4-Nitrophenyl)thio](2,4,6-tri-*tert*-butylphenyl)aminyl (**2a**) and related radicals have been generated and studied by ESR spectroscopy. Radical **2a**, produced by oxidation of *N*-[(4-nitrophenyl)thio]-2,4,6-tri-*tert*-butylaniline (**1a**) with lead dioxide, was isolated as pure dark brown needles in 45% yield and was stable for one month while exposed to air. The molecular structure has been determined by X-ray diffraction analysis. The radical crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.352$ (2) Å, $b = 14.315$ (5) Å, $c = 18.426$ (3) Å, $\beta = 93.23$ (2)°, and $Z = 4$. The structure shows that the nitrogen and sulfur atoms, the *S*-phenyl ring, and the nitro group are almost in the same plane, while the *N*-phenyl ring is 90.7° twisted from the coplane. The S–N bond distance found for **2a** is 1.605 (8) Å, which lies between the typical S–N single and double bond distances. This intermediate bond distance is interpreted in terms of the formation of a three-electron bond between the nitrogen and sulfur atoms.

Free radicals are important intermediates in organic and photochemical reactions and are generally very reactive species. However, electronic stabilizations and steric protections often make them persistent. For instance, 2,2-diphenyl-1-1-picrylhydrazyl,[2] verdazyls,[3] and nitroxide radicals[4] can be isolated as pure crystals or oils. However, such extremely persistent free radicals are rather rare, and most of the free radicals generated so far are transient or have relatively short limited lifetimes under the usual conditions.[5,6] Therefore, it is of considerable interest to prepare a new class of isolable free radicals.

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[1] Part 17 in the series "ESR Studies of Nitrogen-Centered Free Radicals". For part 16, see: Miura, Y.; Nakamura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3217.

[2] Goldschmidt, S.; Renn, K. *Chem. Ber.* **1922**, *55*, 628.

[3] Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 455.

[4] Rozantsev, E. G. "Free Nitroxyl Radicals"; Plenum Press: New York, 1970.

[5] Forrester, A. R.; Hay, J. M.; Thomson, R. H. "Organic Chemistry of Stable Free Radicals"; Academic Press: London, 1968.

[6] Ingold, K. U. "Free Radicals"; Kochi, J. K., Ed; Wiley: New York, 1973; Vol. I, pp 37–112.

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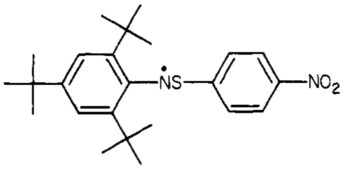
For the few past years we have studied a variety of thioaminyls (RṄSR′) by electron spin resonance (ESR) spectroscopy.[1] These radicals are easily generated by hydrogen abstraction from the appropriate thioamines (RNHSR′) and are persistent in solution. Among them, the particularly interesting ones are (arylthio)(3,5-di-*tert*-butylphenyl)aminyls which can be isolated as pure crystalline dimers which dissociate into the original radicals in solution at room temperature with large equilibrium constants.[7]

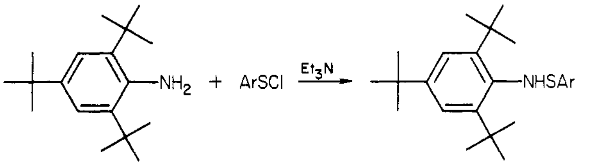
The present study was initiated with the purpose of preparing isolable thioaminyls. This goal was achieved with [(4-nitrophenyl)thio](2,4,6-tri-*tert*-butylphenyl)aminyl (**2a**).[8] In this report we describe the preparation and isolation of **2a**, its ESR parameters, and its X-ray structural analysis.



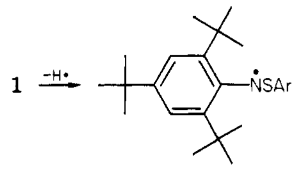
2a

Results and Discussion

N-[(4-Nitrophenyl)thio]-2,4,6-tri-*tert*-butylaniline (**1a**) was obtained as yellow prisms in 46% yield by the reaction of 2,4,6-tri-*tert*-butylaniline with 1 equiv of 4-nitrobenzenesulfenyl chloride. However, when other sulfenyl chlorides such as 4-chloro- and 3,5-dichlorobenzenesulfenyl chlorides were employed in the reaction, no *N*-thioanilines could be obtained in spite of repeated attempts. This reaction is obviously retarded by the steric hindrance due to the *tert*-butyl groups in 2,4,6-tri-*tert*-butylaniline, and the result that **1** could be obtained only when 4-nitrobenzenesulfenyl chloride was employed can be reasonably interpreted in terms of the higher reactivity of the latter sulfenyl chloride. In the cases of 4-chloro- and 3,5-dichlorobenzenesulfenyl chlorides, the reaction mixtures showed a green color and gave ESR signals due to **2b** and **2c**, as described below.



1



2

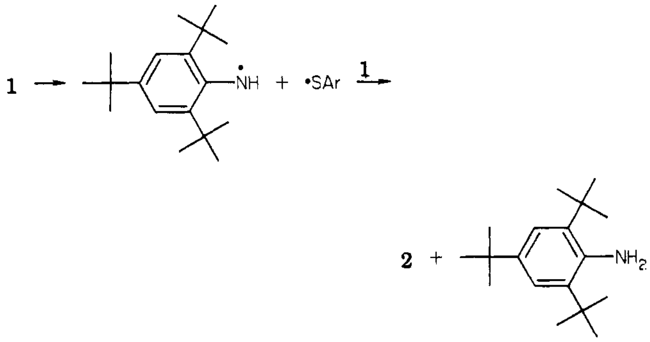
a, Ar = 4-$NO_2C_6H_4$; b, Ar = 4-ClC_6H_4; c, Ar = 3,5-$Cl_2C_6H_3$

The generation of **2a** was performed by the following methods: (a) treatment of **1a** with lead dioxide and potassium carbonate; (b) UV irradiation of solutions containing **1a** alone or **1a** and di-*tert*-butyl peroxide; (c) reaction of **1a** with di-*tert*-butyl diperoxyoxalate. Any of these procedures provided a strong and clean 1:1:1 triplet signal due to **2a**. The hyperfine splitting (hfs) constants and *g* values are listed in Table I. The ESR parameters for the 1:1:1 triplet signals detected from the green reaction mixtures are a_N = 12.27 G, g = 2.0067 and a_N = 12.25 G, g = 2.0064, which are very close to those for **2a**. Thus, we assigned these signals to **2b** and **2c**. The anticipated mechanism for the formation of **2b** and **2c** may be described as follows; thioanilines **1b** and **1c** are probably formed in the reactions of the sulfenyl chlorides with 2,4,6-tri-*tert*-butylaniline, but they are very unstable because of the steric strain caused by the presence of the *tert*-butyl groups, decomposing via the homolytic fission of their S–N bonds to 2,4,6-tri-*tert*-butylanilino[9] and arenethiyl radicals. Since the anilino radical has been shown not to be very reactive due to the steric crowding of the nitrogen, the arenethiyl radicals seem to abstract a hydrogen atom from **1** to produce **2**.

Table I. ESR Parameters for 2 and Related Radicals[a]

radical	a_N	$a_{o\text{-}H}$[b]	$a_{m\text{-}H}$[b]	$a_{p\text{-}H}$[b]	g	temp, °C
2a[c]	12.30				2.0066	19
2a[d]	12.22				2.0065	22
2a[d]	12.20				2.0065	−35
2a[d]	12.15				2.0065	−74
2b[c]	12.27				2.0067	19
2c[c]	12.25	1.20		1.20	2.0064	19
3a[e,f]	9.59	0.78	0.27	0.84	2.0059	room temp
4a[g]	11.89	1.07			2.0068	15

[a] Hyperfine splitting constants are given in gauss. [b] *S*-Phenyl ring protons. [c] Solvent benzene. [d] Solvent hexane. [e] Splitting constants due to the *N*-phenyl ring protons: $a_{o\text{-}H}$ = 3.70 G, $a_{m\text{-}H}$ = 1.26 G, $a_{p\text{-}H}$ = 4.18 G. [f] Taken from ref 15. [g] Taken from ref 16.



The ESR spectra of **2a** and **2b** are split into a simple 1:1:1 triplet by the interaction with a nitrogen nucleus only. On the other hand, in the spectrum of **2c** the 1:1:1 triplet is further split into a 1:3:3:1 quartet by the interaction with the *S*-phenyl ring protons, though the splitting is not complete. All the spectra are broad. For instance, the peak-to-peak line width in the spectrum of **2a** is 3.5 G. This width of lines is probably a consequence of unresolved couplings due to the aromatic and *tert*-butyl protons. Therefore, satellites due to ^{13}C, ^{33}S, and ^{15}N in natural abundance could not be detected.[10]

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

(8) For a preliminary communication of this work, see: Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Chem. Soc., Chem. Commun.* **1980**, 37.

(9) Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 6151 and references cited therein.

(10) In the ESR spectra of related radicals, ArSṄSAr,[11,12] 3,5-(*t*-Bu)$_2$NSAr,[7] *t*-BuṄSN(t-Bu)MRn,[13] ArṄSBu-*t*,[14] and *t*-BuṄSAr,[14] satellites due to ^{13}C, ^{33}S, and ^{15}N, have been observed without any enrichment of the isotopes.

(11) Rolfe, S.; Griller, D.; Ingold, K. U.; Sutcliffe, L. H. *J. Org. Chem.* **1979**, *44*, 3515.

(12) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2395.

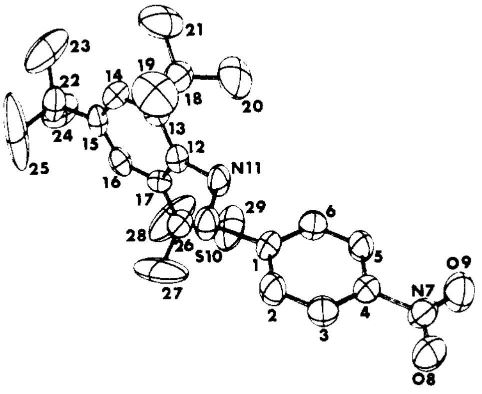


Figure 1. Molecular structure of **2a**.

Radical **2a** was quite persistent in solution and had no tendency to dimerize even at a low temperature (−74 °C). When **1a** was oxidized in benzene with lead dioxide and potassium carbonate under a nitrogen atmosphere, **2a** was almost quantitatively formed and persisted over a long period (~3 days) with little decomposition. Thus, it seemed that the radical was stable enough to be isolated. However, when oxygen was bubbled into the radical solution during 30 min, the dark brown solution turned orange, and no ESR signal was detected from the solution. The decomposition products were very complex, and no product could be isolated.

Isolation of the Radical and Its Properties. Operations for the isolation procedures of **2a** were carried out under oxygen-free conditions in order to avoid the decomposition of the radical which was obtained as dark brown needles in a 45% yield (see the Experimental Section). The crystals are highly soluble in ordinary organic solvents such as benzene, hexane, tetrahydrofuran, chloroform, and acetonitrile and give a dark brown solution from which a strong ESR signal due to **2a** was detected. A visible spectrum of the radical in benzene solution showed λ_{max} at 403, 509 nm (ϵ 1050), 543 (930), and 690 (870). The radical in solution reacted with oxygen as described above but was very stable in the crystalline form even in the presence of oxygen and showed no detectable decomposition on standing for 1 month exposed to the atmosphere.

Crystal Structure of 2a. A crystal structure analysis not only confirms the general correctness of the proposed structure but provides additional interesting structural features of the new compound. The molecular structure of **2a** is shown in Figure 1, and the selected bond distances and angles are given in Figure 2.

The *S*-phenyl ring (A plane) is quite planar, as revealed by the small maximum (0.006 Å) and average (0.004 Å) deviations from the least-squares plane. On the other hand, the *N*-phenyl ring (B plane) is less planar, as shown by the relatively large maximum (0.038 Å) and average (0.022 Å) deviations from the least-squares plane. This less planar feature of the *N*-phenyl ring is probably attributable to the steric effects due to the *tert*-butyl groups. The maximum deviation from the plane through the C(1), S(10), N(11), and C(12) atoms (C plane) is only 0.007 Å, indicating that the four atoms are almost in the same plane. Similarly, the plane through the C(4), N(7), O(8), and C(9) atoms (D plane) is also very planar, as shown by the small maximum deviation of 0.004 Å. Interestingly, the dihedral angle between the least-squares A and C planes is only 0.1°, and that between the A and D planes is 0.6°. Accordingly, the A, C, and D planes are almost in the same plane. However, the B plane is perpendicular to the coplane, as indicated by the dihedral angle of 90.7° between the A and B planes, suggesting that the *N*-phenyl ring has no ability to delocalize the unpaired electron.

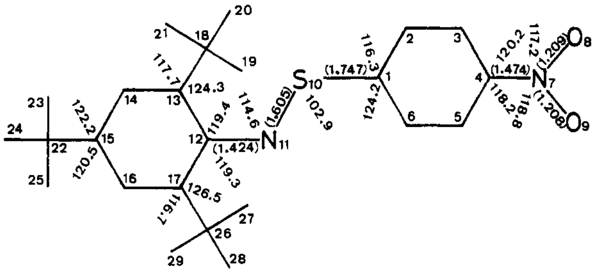
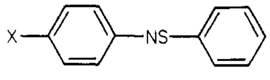
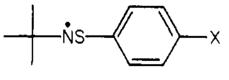


Figure 2. Selected bond distances (Å) and bond angles (deg) for **2a**. Bond distances are given in parentheses.

This twisted structure of **2a** clarified by the X-ray diffraction analysis is well reflected upon the ESR parameters for **2**. As can be seen in Table I, the nitrogen hfs constants for **2** are 2.7 G larger than that for **3a**[15] which would adopt a planar structure, and are rather close to those (11.70–11.89 G) for (arylthio)-*tert*-butylaminyls (**4**)[16] in which the *N*-phenyl ring in **2** has been replaced with a *tert*-butyl group having no or little ability to delocalize the unpaired electron. Also, in the spectrum of **3a** the splitting of 1.26 G due to the *N*-phenyl meta protons is observed, whereas in **2** no such a splitting is detectable. Furthermore, the splitting of 1.20 G due to the *S*-phenyl ring protons in **2** is 0.36 G larger than that for **3a**. From these ESR results we conclude that in **2** the unpaired electron is not or little delocalized onto the *N*-phenyl ring, in contrast to the case of **3** in which the unpaired electron is delocalized to a great extent onto the *N*-phenyl ring, and this is in good agreement with the twisted structure of **2**.



3 (3a, X = H)



4 (4a, X = NO$_2$)

The S–N bond distance of 1.605 (8) is of particular interest. In Table II this bond distance is compared with the S–N single and double bond distances in compounds such as **5**,[17] **6**,[18] **7**,[19] **8**,[20] and **9**.[21] As found in Table II, the S–N bond distance for **2a** is considerably shorter than the S–N single bond distances for **5** and **6** but is longer than the S–N double bond distances, indicating that the S–N bond distance for the radical lies between S–N single and double bond distances.

In radicals **2**, the unpaired electron resides formally in the nitrogen 2p$_z$ orbital, with a lone pair of electrons on the adjacent sulfur atom. When a stabilizing interaction is possible between the singly occupied orbital on nitrogen and the doubly occupied nonbonding orbital on the heteroatom, that is, the energy gap between the two orbitals

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(13) Brunton, G.; Taylor, J. F.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 4879.

(14) Unpublished results.

(15) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142.

(16) Miura, Y.; Asada, H.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1855.

(17) Tamura, C.; Aiba, K.; Sato, S.; Hata, T.; Morimura, S.; Yoshioka, T. *Acta Crystallogr., Sect. B* **1977**, *33*, 3918.

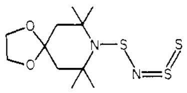
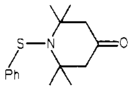
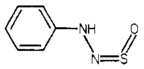
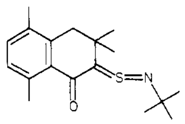
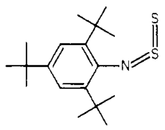
(18) Sato, S.; Yoshioka, T.; Tamura, C. *Acta Crystallogr., Sect. B* **1975**, *31*, 1385.

(19) Gieren, A.; Dederer, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 179.

(20) Schepper, L.; Nielsen, K.; Norrestam, R. *Acta Crystallogr., Sect. B* **1978**, *34*, 2940.

(21) Iwasaki, F. *Acta Crystallogr., Sect. B* **1979**, *35*, 2099.

Table II. Comparison of the S-N Bond Distance for 2a with Some S-N Single and Double Bond Distances in the Literature

compd	S-N single bond[a]	S-N double bond[a]	ref
 **5**	1.634, 1.657	1.569	17
 **6**	1.694		18
 **7**		1.560	19
 **8**		1.558	20
 **9**		1.548	21
2a	1.605 (8)[b]		this work

[a] Given in angstroms. [b] Estimated standard deviation is given in parentheses.

is relatively small and the overlap between the orbitals is not too large, a three-electron bond between the atoms would be formed, resulting in the stabilization of the radical.[22] In three-electron bonds, two of the three electrons are in a bonding orbital, and the third is in an energetically close antibonding orbital, leading to the formation of an intermediate bond distance. It seems that such an intermediate bond distance found for **2a** can be reasonably interpreted by this consideration, similar to the $>\dot{N}-\dot{O}$ bonds in nitroxide radicals[4] and the $\dot{N}-\ddot{O}$ bonds in $R\dot{N}OR'$ radicals.[23] In fact, ab initio molecular orbital calculations on the $H-\dot{N}-SH$ radical using a double ζ basis set predicted the formation of a three-electron bond between the nitrogen and sulfur.[24]

$$-\dot{N}-\ddot{S}- \longleftrightarrow -\ddot{N}^{-}-\dot{S}^{+}- \text{ or } -N\overset{\cdots}{-}S-$$

Radicals **2** seem to be significantly strained, owing to the presence of *tert*-butyl groups. For example, the C(12)–C(13)–C(18) bond angle of 124.3° is 6.6° larger than the opposite C(14)–C(13)–C(18) angle, and the C(12)–C(17)–C(26) bond angle of 126.5° is 9.8° larger than the C(16)–C(17)–C(26) angle. We consider that these deviations in bond angle from the 120° value expected for an sp^2 carbon can be attributable to the steric repulsion between the *o*-*tert*-butyl groups and the N(11) atom, as judged by the relatively short intermolecular nonbonding distances for N(11)···C(20) (2.823 Å) and N(11)···C(29) (2.849 Å). Accordingly, it seems that there is a large crowd of atoms around the radical center; this crowd of atoms would play an important role in the protection of the radicals from decomposition and would also prevent dimerization of the radicals.

Experimental Section

Melting points were taken on a Yanagimoto MP micro-melting-point apparatus and are uncorrected. Infrared (IR) spectra were run on a JASCO Model IR-G spectrometer. Visible and proton magnetic resonance (^1H NMR) spectra were recorded with Hitachi 220 and Hitachi Perkin-Elmer R-20 spectrometers, respectively. Chemical shifts were measured relative to tetramethylsilane (δ 0). Elemental analyses were performed on a Yanagimoto MT-2 CHN recorder.

4-Chloro- and 4-nitrobenzenethiols were obtained commercially. 3,5-Dichlorobenzenethiol,[25] 2,4,6-tri-*tert*-butylaniline,[26,27] and di-*tert*-butyl diperoxyoxalate[28] were prepared by the reported methods. 4-Chloro-, 3,5-dichloro-, and 4-nitrobenzenesulfenyl chlorides were obtained by the usual method[7] and were used without further purification. Lead dioxide was purified by the previously reported method.[7]

***N*-[(4-Nitrophenyl)thio]-2,4,6-tri-*tert*-butylaniline (1a).** 4-Nitrobenzenesulfenyl chloride, prepared from 2.53 g (16 mmol) of 4-nitrobenzenethiol, was dissolved in 50 mL of dry diethyl ether (ether), and the solution was added to a stirred solution of 2,4,6-tri-*tert*-butylaniline (4.30 g, 16 mmol) and triethylamine (2.5 g, 25 mmol) in dry ether (300 mL) and −5–0 °C. After addition of the sulfenyl chloride solution, the reaction mixture was stirred for 5 h at room temperature. Filtration of the reaction mixture and evaporation of the solvent gave a yellow powdery residue, which was chromatographed an alumina (E. Merck, Art 1097; column size 3 × 30 cm) with benzene–hexane (1:4). The second yellow zone was collected, and the solvent was evaporated to give yellow crystals **1a** (2.93 g, 46%), which were recrystallized from hexane and then methanol to provide yellow prisms: mp 152–153 °C: IR(KBr) 3300 (NH), 2900–2800, 1590, 1570, 1510, 1470, 1420, 1390, 1360, 1330, 1210, 1100, 1080, 890, 880, 850, 840, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, *p*-*t*-Bu, 9 H), 1.50 (s, *o*-*t*-Bu, 18 H), 5.20 (s, NH, 1 H), 7.23–8.23 (m, aromatic, 6 H).

Anal. Calcd for $C_{24}H_{34}N_2O_2S$: C, 69.53; H, 8.27; N, 6.76. Found: C, 69.64; H, 8.27; N, 6.78.

[(4-Nitrophenyl)thio](2,4,6-tri-*tert*-butylphenyl)aminyl (2a). Thioaniline **1a** (0.10 g, 0.24 mmol) and potassium carbonate (0.5 g) in dry benzene (10 mL) were stirred for 10 min under nitrogen. To the stirred mixture was added, by portions over an interval of 10 min, under a nitrogen stream, 0.5 g of lead dioxide [the conversion into **2a** was checked by thin-layer chromatographic analysis: alumina (E. Merck, Art 1064); eluant benzene–hexane (1:10)]. The resultant dark brown mixture was quickly filtered, and the solvent was removed by freeze–drying, giving a dark brown crystalline residue. Then, to the residue was added 2 mL of methanol, and it was cooled to 0 °C under a nitrogen atmosphere to give dark brown needles, which were filtered and recrystallized from 5 mL of methanol under nitrogen; mp 127–129 °C (in a degassed capillary); 45% yield; IR (KBr) 2900–2800, 1580, 1560, 1500, 1460, 1400, 1380, 1350, 1320, 1280, 1210, 1110, 1100, 1070, 870, 850, 740 cm^{-1}; UV λ_{max} (benzene) 403, 509 nm (ε 1050), 543 (930), 690 (870).

Anal. Calcd for $C_{24}H_{33}N_2O_2S$: C, 69.64; H, 8.04; N, 6.77. Found: C, 69.72; H, 8.11; N, 6.80.

Although the preparation of *N*-[(4-chlorophenyl)thio]- (**1b**) and *N*-[(3,5-dichlorophenyl)thio]-2,4,6-tri-*tert*-butylanilines (**1c**) was attempted in a manner similar to that for **1a**, both compounds could not be obtained in spite of repeated experiments. For ESR measurements of **2b** and **2c**, the concentrates of the mixtures

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obtained from the reactions of the sulfenyl chlorides with 2,4,6-tri-*tert*-butylaniline were employed.

ESR Measurements. Radical **2a** was generated in benzene or hexane by the following procedures: (a) treatment of **1a** with lead dioxide and potassium carbonate; (b) UV photolysis of **1a** alone or in the presence of di-*tert*-butyl peroxide; (c) reaction of **1a** with di-*tert*-butyl diperoxyoxalate. The UV photolysis was carried out by using a JEOL JES-UV-1 apparatus. All ESR samples were carefully deoxygenated by three freeze–thaw–pump cycles. ESR spectra were recorded on a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and g values were determined by comparison with those for Fremy's salt in K_2CO_3 aqueous solution (a_N, 13.09 G; g, 2.0057).

Crystal data for 2a: monoclinic, $a = 9.352$ (2) Å, $b = 14.315$ (5) Å, $c = 18.426$ (3) Å, $\beta = 93.23$ (2)°, $V = 2462.8$ Å, $Z = 4$, $d_{calcd} = 1.12$ g cm^{-3}. Systematic absences for $0k0$, $k = 2n + 1$ and $h0l$, $l = 2\ n + 1$ established the space group as $P2_1/c$. The cell dimensions were obtained by a least-squares refinement of 15 reflections on a Rigaku AFC5 apparatus equipped with a rotating-anode X-ray generator and using a graphite monochrometer (λ(Cu Kα) = 1.5418 Å).

Solution and Refinement of the Structure of 2a. A single crystal of approximate dimensions 0.35 × 0.15 × 0.10 mm was used for the 2θ–θ scan data collection ($2\theta \leq 128°$). Three reflections were monitored every 100 reflections, and the examination at the end of the data collection showed no sign of crystal decomposition. The data were corrected for Lorentz and polarization effects but not for absorption. Among the 4274 unique reflections collected, 1820 were considered to be observed at the $2.5\sigma(F_0)$ level.

The structure was solved with MULTAN 74[29] and was refined by block-diagonal least-squares methods. On the difference maps, 27 hydrogen atoms were found. Positions of the remaining hydrogen atoms were estimated from standard geometry. The final refinements, with anisotropic temperature factors for heavy atoms and isotropic temperature factors for hydrogen atoms, were 0.086 for R and 0.081 for R_w.[30] The final value of $[\sum w(|F_0| - |F_c|)^2(m - n)]^{1/2}$, where m is the number of observation and n is the number of variables, was 2.34. In these calculations anomalous dispersion corrections were applied to the scattering factors of S, O, and N atoms.[31]

Registry No. 1a, 70741-37-6; **2a**, 70741-30-9; **2b**, 62991-72-4; **2c**, 81536-47-2; 2,4,6-tri-*tert*-butylaniline, 961-38-6; 4-nitrobenzenesulfenyl chloride, 937-32-6; 4-chlorobenzenesulfenyl chloride, 933-01-7; 3,5-dichlorobenzenesulfenyl chloride, 74282-78-3.

Supplementary Material Available: Tables listing final values of atomic coordinations (Table II), anisotropic thermal parameters (Table III), hydrogen atom parameters (Table IV), bond distances (Table V), and bond angles (Table VI) and an ESR spectrum for **2a** (6 pages). Ordering information is given on any current masthead page. Lists of observed and calculated structure factor amplitudes for **2a** are available from the authors.

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Reduction of Organic Halides by Water and Zinc Effected by Nickel

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A new method for the reduction of a variety of organic halides has been developed. The reaction takes place under mild conditions and employs water, zinc, and a catalytic amount of nickel chloride, triphenylphosphine, and iodide ion. The reduction of *p*-chloroanisole by this method was investigated in some detail. The reaction rate was first order in nickel and aryl halide but independent of the water concentration. A brief mechanism of this reaction is presented.

There are a number of methods for the hydrogenolysis of carbon–halogen bonds using transition-metal catalysts.[1] Recent attention has centered on the use of hydride sources in conjunction with transition metals to effect reduction of organic halides. Ashby and Lin reported that mixtures of $LiAlH_4$ with stoichiometric or catalytic amounts of $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ are effective in removal of halo or tosylate groups from organic compounds.[2] Bis(triphenylphosphine)nickel chloride has been demonstrated to be an efficient reduction catalyst when used in conjunction with sodium borohydride,[3] and palladium(0) with sodium methoxide,[4a] sodium formate,[4b] and triethylammonium formate[5] as hydride sources has been used in the reduction of aryl halides. All of the above methods suffer from some disadvantages. The use of powerful hydride sources such as $LiAlH_4$ and $NaBH_4$ leads to low selectivity, since these reagents are capable of reducing a number of other functional groups. Palladium is very expensive and does not react with as wide a variety of organic halides as nickel.

It is known that a mixture of nickel(II) salt, triphenylphosphine, and a reducing agent (such as zinc) in a dipolar aprotic solvent such as DMF will generate zero-valent tris(triphenylphosphine)nickel.[6,7] This highly air-sensitive reagent is able to oxidatively add a large number of organic halides[8-10] to form intermediates which

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