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Chemistry of *N*-Thiosulfinylanilines. II.[1] Thermolysis and Photolysis of *N*-Thiosulfinylanilines

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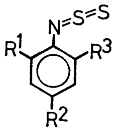
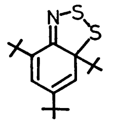
Thermolysis of 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**1**) in refluxing benzene afforded 2,4-di-*t*-butyl-8-thia-9-azabicyclo[4.3.0]nona-2,4,6,9-tetraene (**6**) and 2,4-di-*t*-butyl-6-methylaniline (**7**), while its photolysis resulted in the formation of *N*,*N'*-bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur diimide (**17**) and **7**. The mechanism of the thermolysis involving 1,5-hydrogen migration and *o*-quinonoid intermediate has been proposed. The electronic spectrum of the initial intermediate in the photolysis was obtained in EPA matrix and tentatively assigned to a dithionitro compound (**42**) or a dithiaziridine (**41**). Thermolysis of 2,4,6-tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]nona-2,4,9-triene (**4b**) equilibrated with 2,4,6-tri-*t*-butyl-*N*-thiosulfinylaniline (**4a**) gave 4,6-di-*t*-butyl-3*H*-1,2,3-benzodithiazole 2-oxide (**26**) and 2,4,6-tri-*t*-butylaniline (**27**). The reaction in the presence of a catalytic amount of *p*-toluenesulfonic acid improved the yield of both **26** and **27**, suggesting the ionic decomposition pathway. However, an ESR signal was observed during the thermal decomposition of **4** in the absence of oxygen, implying a concurrent homolytic pathway if not a major one. The mechanism of these reactions are briefly discussed. The photolysis of **4** led to **27** and *N*,*N'*-bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur diimide (**43**).

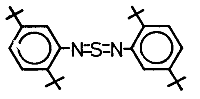
In a previous paper,[1] we described the preparation of sterically hindered *N*-thiosulfinylanilines (**1**—**4**) by the reactions of the corresponding anilines with disulfur dichloride. Of these, **1** is a stable crystalline compound, while **2** and **3** are unstable at ambient temperature.



1 $R^1=R^2=t\text{-Bu}, R^3=Me$
2 $R^1=R^2=t\text{-Bu}, R^3=i\text{-Pr}$
3 $R^1=R^2=R^3=Me$
4a $R^1=R^2=R^3=t\text{-Bu}$



4b



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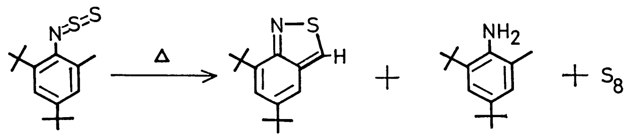
Furthermore, **4a** exists as a cyclized form (**4b**) in the solid state and an equilibrium between **4a** and **4b** is established in solution. In the case of 2,5-di-*t*-butylaniline, the product was not the *N*-thiosulfinylaniline but the sulfur diimide (**5**).

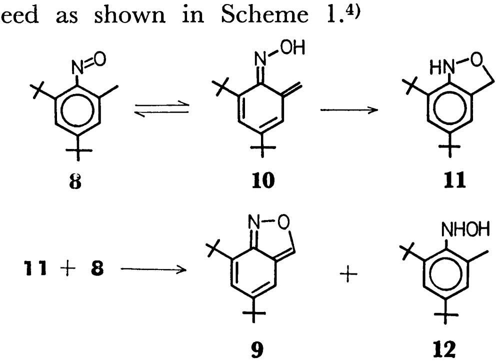
We disclose in this paper the thermal and photochemical behaviors of **1** and **4** and discuss the factors influencing the thermal stabilities of these *N*-thiosulfinylanilines.[2]

Results and Discussion

Thermolysis of N-*Thiosulfinylaniline (1).* Heating **1** in refluxing benzene for 21 h gave 2,1-benzisothiazole (**6**) (32%), the corresponding aniline (**7**) (26%), and sulfur. When the reaction was conducted in toluene at 70 °C (28 h), the yields of **6** and **7** were 40% and 46%, respectively.



During the reaction a trace of hydrogen sulfide was detected (as PbS). This reaction is reminiscent of the thermolysis of 2,4-di-*t*-butyl-6-methylnitrosobenzene (**8**) leading to **9** and **7**,[3] which was found by us to proceed as shown in Scheme 1.[4]

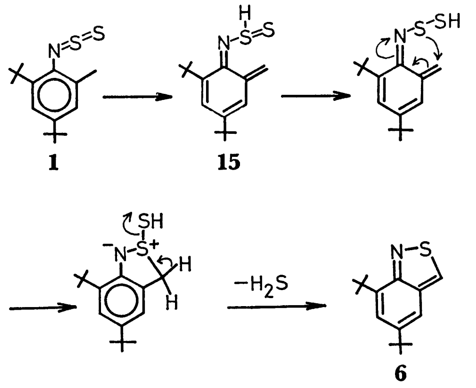


$\mathbf{11} + \mathbf{12} \longrightarrow \mathbf{9} + \mathbf{7} + H_2O$

Scheme 1.

Furthermore, 2,4-di-*t*-butyl-6-ethyl- (**13**) and 2,4-di-*t*-butyl-6-isopropylnitrosobenzenes (**14**) have been found to be less stable than **8** to decompose even at 0—5 °C;[4] this order of stability is consistent with the above scheme in which the decomposition starts with 1,5-hydrogen shift, for the initially formed *o*-quinone imine (**10**) is thought to be more stable for **13** or **14** than for **8**.

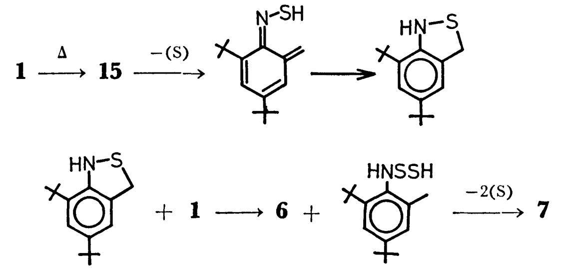
Considering the similar order of stability observed in the case of *N*-thiosulfinylanilines (*i.e.*, **2** is less stable than **1**), the following mechanism (Scheme 2) starting with 1,5-hydrogen shift seems to be the most probable pathway also here.



$\mathbf{1} + H_2S \longrightarrow \mathbf{7} + 3S$

Scheme 2.

The last step (reduction of **1** with hydrogen sulfide) was confirmed by a separate experiment.



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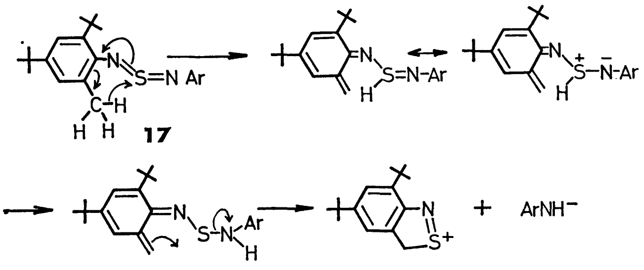
Scheme 3.

The following alternative pathway (Scheme 3) involving the thiooxime is also possible; extrusion of sulfur from such types of compounds as **15** and **16** are known.[5] However, there is no experimental evidence so far to distinguish these two mechanisms. Whichever mechanism is operative, these pathways starting with 1,5-hydrogen shift explain the instability of *N*-thiosulfinylanilines with ortho benzylic hydrogens.

Such a 1,5-hydrogen shift involving ortho benzylic hydrogens seems a general type of reaction; sulfur diimide (**17**) obtained by the photolysis of **1** (*vide infra*) cleanly disproportionated (refluxing benzene, 3 h) to yield **6** (94%) and **7** (91%). Essentially the same results were obtained also in refluxing methanol, the yields of **6** and **7** being 97 and 87% respectively.

$$\underset{\mathbf{17}}{\text{Ar-N=S=N-Ar}} \longrightarrow \mathbf{6} + \mathbf{7} \qquad \text{Ar}=2,4\text{-}(t\text{-Bu})_2\text{-}6\text{-MeC}_6\text{H}_2$$

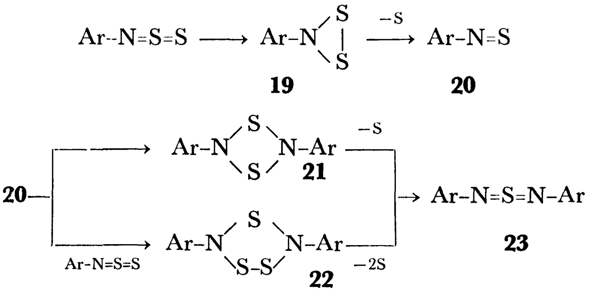
This new mode of reaction of sulfur diimide presumably proceeds also *via* 1,5-hydrogen shift from methyl group to sulfur atom followed by prototropy and cyclization as depicted in Scheme 4.



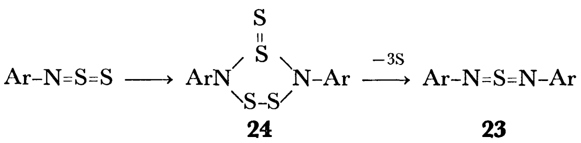
⟶ **6** + **7**   Ar = 2,4-(*t*-Bu)$_2$-6-MeC$_6$H$_2$

Scheme 4.

In connection with the thermal behavior of **1**, it is an interesting problem why the reaction product of 2,5-di-*t*-butylaniline with disulfur dichloride is sulfur diimide (**5**) instead of the *N*-thiosulfinylaniline **18** which would be no doubt the initial product. There are two conceivable routes leading to **5**. The one (Scheme 5) proceeds *via* three-membered ring isomer (**19**), which loses a sulfur atom to give thionitroso compound (**20**), followed by dimerization to give **21** or by cycloaddition to thiosulfinylamino group to give **22**. Subsequent extrusion of sulfur from **21** or **22** would lead to sulfur diimide (**23**). Another route consists of dimerization of the *N*-thiosulfinylaniline followed by extrusion of sulfur (Scheme 6).

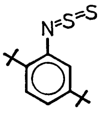


Scheme 5.



Scheme 6.

Cyclization to three-membered ring followed by extrusion of a sulfur atom has been commonly observed for other thiocumulenes: thiocarbonyl ylides give olefins,[6] thiocarbonylimines give imines,[7] a sulfine gives a ketone,[8] and *N*,*N*′-diphenylsulfur diimide gives azobenzene.[9] Cyclic sulfur imides such as **21** or **22** with six or less than six-membered ring appear to be unstable.[10] Bulky groups around the thiosulfinylamino group may hinder the formation of three-membered ring isomer (**19**) as well as dimerization to **24**. These considerations can thus explain the instability of **18** compared to **1**—**4**.



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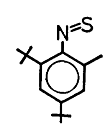

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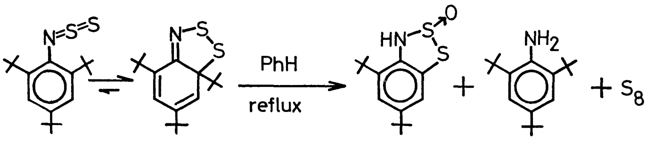
Thermolysis of **1** into **6** and **7** may be rationalized also in terms of an intermediacy of (thionitroso)benzene (**25**), which would give **6** and **7** quite similarly to the case of nitrosobenzene **8** (Scheme 1). A mercaptoamine, thio analog of **12**, is known to lose the sulfur atom to give the corresponding amine.[5a] Alternatively, formation of the sulfur diimide **17** followed by its disproportionation is also a possible route giving **6** and **7**. However, these two pathways involving the formation of **25** cannot explain the fact that 6-isopropyl derivative **2** is less stable than 6-methyl derivative **1**.

Taken together, we consider that *N*-thiosulfinylanilines decompose *via* pathways starting with 1,5-hydrogen shift if steric protection of a thiosulfinylamino group is sufficient and benzylic hydrogens are present in the ortho substituent. In the case where steric protection is insufficient, the *N*-thiosulfinylanilines would undergo decomposition into the thionitroso intermediate (**20**) *via* cyclization into the dithiaziridine (**19**) to give the sulfur diimide as the final product.

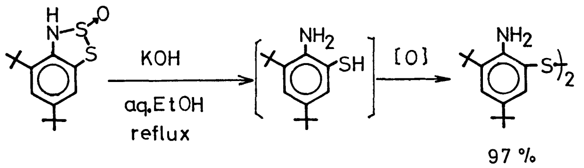
Thermolysis of N-*Thiosulfinylaniline (**4a**) Equilibrated with 1,2,3-Dithiazole (**4b**).* The above argument suggests that an *N*-thiosulfinylaniline with enough steric protection and with no ortho benzylic hydrogen would enjoy considerable thermal stability. Thus, we have examined the thermolysis of **4a** which not only meets these requirements, but also is in equilibrium with **4b** with the latter as a major component.[1]

Thermolysis of **4** in refluxing benzene under nitrogen for 9.7 h gave **26** (20.6%), **27** (34.2%), and sulfur (27%).

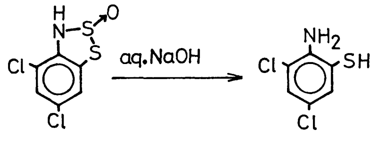


4a **4b** **26** **27**

The structure of **26** was determined by the elemental analysis, the spectral data, and the following chemical behavior. Alkaline hydrolysis of **26** followed by chromatography gave the disulfide (**28**), suggesting the 2-oxide structure of **26**; a similar hydrolysis of **30** into **31** has been reported.[11] In the present case, **29**, a primary product, is thought to be oxidized into **28** during the work-up procedure.

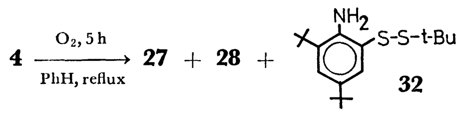


26 **29** **28**

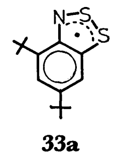


30 **31**

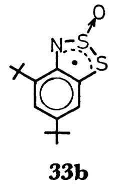
Thermolysis of **4** in the presence of a catalytic amount of *p*-toluenesulfonic acid improved the yield of **26** and **27** up to 39.0 and 56.1%, respectively, with 71% conversion. However, thermolysis of **4** under a stream of oxygen gave a complex reaction mixture, from which **27** (11.5%), **28** (12.2%), and **32** (9.5%) were isolated but no **26** was obtained.



Thermolysis of **4** in degassed benzene at 110 °C for 5 min afforded a persistent ESR signal (a_N=8.2 G,



33a



33b

g=2.008) as shown in Fig. 1. This signal was considered to be due to a nitrogen-centered radical **33a**, although alternative structure **33b** cannot rigorously be excluded. In any case, the large *g*-value (2.008) suggests that an unpaired electron is delocalized on two sulfur atoms as in the case of **34**,[12] for which a large *g*-value (2.0082) was reported.

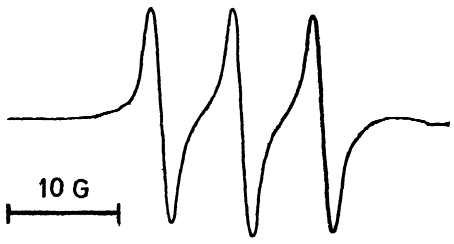


Fig. 1. An ESR spectrum of **33a**.

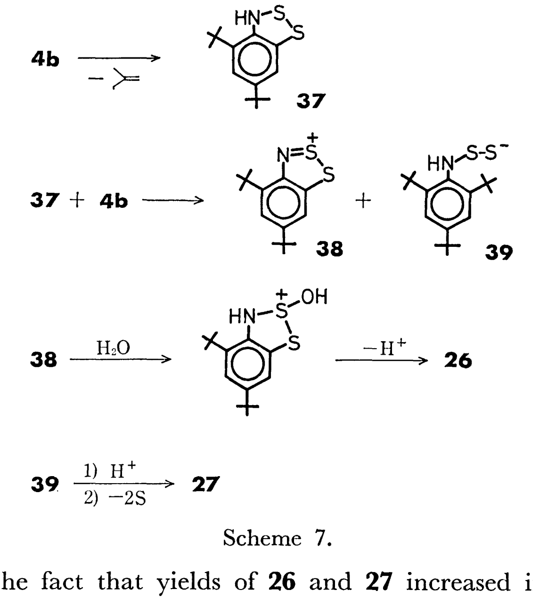
TABLE 1. ESR DATA OF SOME NITROGEN CENTERED RADICALS

Radical	a_N (G)	g
33a	8.2	2.008
Ph-S-$\dot{N}$-S-Ph (**34**)	11.41	2.0082
Ph-$\dot{N}$-S-Ph (**35**)	9.59	2.0059
Ph-S-$\dot{N}$-*t*-Bu (**36**)	11.70	2.0069

Ph-S-$\dot{N}$-S-Ph
34

The hyperfine splitting constant (hfsc) due to a nitrogen nucleus of **33a** (8.2 G) is smaller than those of **34**,[12] **35**,[13] and **36**[14] (see Table 1) suggesting the extensive delocalization of an unpaired electron into the aromatic ring and two sulfur atoms due to the planarity of the molecule.

Although the mechanism to form **26** and **27** is obscure, the following pathway shown in Scheme 7 is conceivable. Elimination of 2-methylpropene from **4b** by retro-ene reaction gives **37**, which reduces **4b** to give **38** and **39**. Then **39** may be unstable and loses the sulfur atoms to give **27** on protonation, while **38** reacts with moisture in a solvent to give **26** on deprotonation.



Scheme 7.

The fact that yields of **26** and **27** increased in the presence of a small amount of the acid is consistent with the above scheme, since formation of **37** appears to be catalyzed by acid.

The following free radical mechanism (Scheme 8) is also conceivable, in view of the observation of an ESR

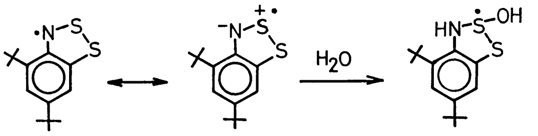
Table 2. Yields of the photolysis products of **1**

Solvent	Concentration (g/l)	Irradiation time (h)	Isolated yields (%) **17**	**7**	S_8
Pentane	4.7	35.3[a)]	70.9	26.5	16.0
Pentane	0.7	9[b)]	42.4	17.1	11.2
Benzene	4.8	30[a)]	34.7	25.3	23.4
2-Propanol	4.7	32[a)]	36.8	28.5	19.8

a) 100 W lamp. b) 400 W lamp.

signal of what is believed to be **33a** although its importance is probably minor. The fact that the presence of oxygen did not favor the formation of **26** suggests that oxygen atom in **26** did not come from atmospheric or dissolved oxygen molecule, but from moisture in the solvent.

$$\mathbf{4b} \xrightarrow{-t\text{-Bu}\cdot}$$



33a

$$\xrightarrow{-\text{H}\cdot} \mathbf{26}$$

$$\mathbf{33a} \xrightarrow{\text{H}\cdot} \mathbf{37} \xrightarrow{\mathbf{4b}} \mathbf{38} + \mathbf{39}$$

Scheme 8.

Photolysis of N-*Thiosulfinylaniline (1) and Related Compounds.* Photolysis of organic thiocumulenes of type X=S=Y has not been reported except for that of thiobenzophenone *S*-oxide, whose products are benzophenone and sulfur.[15)]

Irradiation of **1** with Pyrex-filtered light from a medium pressure mercury lamp below 25 °C afforded the sulfur diimide (**17**), aniline (**7**), and sulfur. The yields and conditions are summarized in Table 2.

$$\underset{\mathbf{1}}{\text{Ar-N=S=S}} \xrightarrow{h\nu} \underset{\mathbf{7}}{\text{ArNH}_2} + \underset{\mathbf{17}}{\text{Ar-N=S=N-Ar}} + \text{S}_8$$

$$\text{Ar}=2,4\text{-}(t\text{-Bu})_2\text{-6-MeC}_6\text{H}_2$$

Irradition of **1** in EPA matrix was carried out at 77 K, and the change in the electronic spectra was monitored intermittently. Recorded spectra are shown in Fig. 2. During irradiation, the intensity of absorption at 340 nm decreased, while a very intense band appeared at 473 nm; isosbestic points were observed at 300 and 355 nm suggesting the species showing an absorption at 473 nm arose directly from **1**. Molar extinction coefficient of this species was estimated to be *ca.* 15000 or more on the basis of the increase of the absorption at 473 nm and the decrease of the absorption at 340 nm. Since absorption due to the nitrene **40** would be around 400 nm or below with the molar extinction coefficient of a few hundreds,[16)] and sulfur atom or its oligomers have their absorption below 420 nm,[17)] neither of these is responsible for the absorption at 473 nm. Consequently, unlike the photolysis of azides, where a nitrene is formed by elimination of nitrogen molecule, simultaneous elimination of two sulfur atoms from thiosulfinylamino group to give a nitrene can be excluded. The absorption at 473 nm may be due to one of three species (**25**, **41**, and **42**), although we have no experimental evidence to determine which is correct. In view of the well

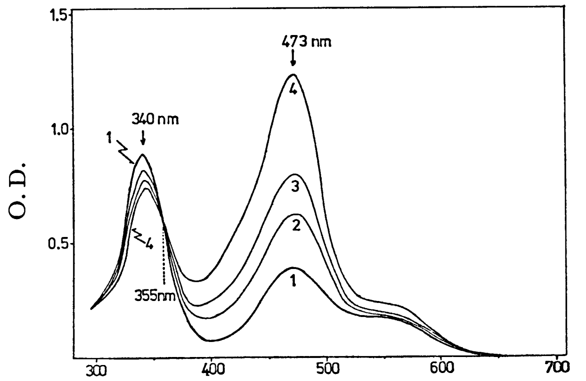
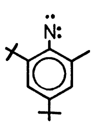


Fig. 2. Change in the electronic spectra of **1** during irradiation.



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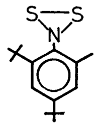

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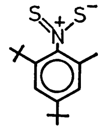

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known tendency of thiocumulenes to extrude sulfur *via* a three-membered ring in photolysis and thermolysis,[6–9,15,18)] it is reasonable to assume that **1** would change into **41** or **42** at first, then loses one sulfur to give **25**, which further reacts through pathways depicted in Scheme 5.

The aniline **7** is probably formed from photodecomposition of **17** because irradiation of **17** in pentane for 33 h gave 18.2% of **7** with recovery of **17** (68.3%). As shown in Table 3, the product ratio **7**/**17** decreases with increasing concentration. The reason for this concentration effect is not clear to us, but one explanation seems due to self quenching of **17**.

Table 3. Concentration effect of the photolysis of **1** in pentane

Concentration (g/l)	Irradiation time (h)	Molar ratio **7/17**
0.67	4	1.1
3.3	11.5	0.58
16.7	24.5	0.27

Photolysis of 4. Irradiation of **4** in pentane afforded sulfur diimide (**43**) (7.5%) and aniline (**27**) (10.5%) together with some unidentified products. Since these products are very similar to those of the photoreaction of *N*-thiosulfinylaniline (**1**), the precursor of these products is considered to be the *N*-thiosulfinylaniline (**4a**).

$$\begin{array}{c}\mathbf{4a}\\ \downarrow\uparrow\\ \mathbf{4b}\end{array} \xrightarrow{h\nu} \underset{\mathbf{27}}{\text{Ar-NH}_2} + \underset{\mathbf{43}}{\text{Ar-N=S=N-Ar}}$$

$$\text{Ar}=2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2$$

Experimental

All melting points were uncorrected. The IR, UV, NMR, and mass spectra were taken with the same spectrometers as used in a previous paper.[1] ESR spectra were recorded with JEOL JES-ME spectrometer. Reactions were carried out under nitrogen unless otherwise stated.

*Thermolysis of 2,4-Di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**1**).* *N*-Thiosulfinylaniline (**1**)[1] (404 mg, 1.44 mmol) was heated for 21 h in refluxing benzene (20 ml). Removal of the solvent followed by dry column chromatography (DCC) (silica gel, hexane) afforded 38 mg of sulfur in the first fraction. From the second fraction, 15 mg (3.7%) of **1** was recovered. The third fraction was rechromatographed (silica gel, CCl_4) to give 115 mg (32.3%) of 2,4-di-*t*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (**6**) which was identified by the IR, NMR, and mass spectra (mp 52—53.5 °C, recrystallized three times from methanol). Spectral and analytical data of this compound are listed in the description of thermolysis of *N,N'*-bis(2,4-di-*t*-butyl-6-methylphenyl)-sulfur diimide (**17**) (*vide infra*). The fourth fraction gave 81 mg (25.6%) of 2,4-di-*t*-butyl-6-methylaniline (**7**) which was identified by comparison of the IR and NMR spectra with those of the authentic sample.[19]

In a similar reaction, when nitrogen stream passed through the refluxing solution was led into aq lead(II) acetate, slight darkening of the solution was observed.

Heating of **1** (401 mg, 1.42 mmol) in toluene (10 ml) at 70 °C for 28 h gave 46.2% of **8**, 39.9% of **6**, and 50 mg of sulfur after a similar work-up.

Thermolysis of N,N'*-Bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur Diimide (**17**).* Compound **17** (224 mg, 0.48 mmol) was heated for 3 h in refluxing benzene (15 ml). After removal of the solvent, the residue was chromatographed (silica gel, hexane). The first fraction gave 112 mg (94.3%) of **6** as white crystals (mp 49—52 °C), which were recrystallized three times from methanol at −78 °C to give colorless prisms, mp 52.5—53.0 °C; IR (KBr): 3080, 2900, 1358, 1245, and 745 cm^{-1}; NMR (CCl_4): δ 1.38 (s, 9H), 1.60 (s, 9H), 7.34 (ABq, J=2 Hz, $\Delta\delta$=0.14, 2H), and 8.92 (s, 1H); $\lambda_{\max}^{\text{hexane}}$ (ε): 232 (26900), 289.5 (8310), 300.5 (9960), and 324 nm (5230); *m/e*: 247 (M^+, 21.7%), 232 (100), 205 (12), 204 (16), 190 (15), 176 (19), 57 (16), and 41 (11). Found: C, 72.64; H, 8.64; N, 5.64; S, 12.88%. Calcd for $C_{15}H_{21}NS$: C, 72.82; H, 8.56; N, 5.66; S, 12.96%.

The second fraction gave 96 mg (91.2%) of **7**.

Thermolysis of **17** (319 mg, 0.683 mmol) in refluxing methanol (140 ml) followed by similar work-up afforded **6** (164 mg, 97.1%) and **7** (130 mg, 86.8%).

*Thermolysis of 2,4,6-Tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]-nona-2,4,9-triene (**4b**).* Heating of **4b** (481 mg, 1.49 mmol) in refluxing benzene (25 ml) for 9.7 h gave orange solution. Removal of the solvent followed by treatment with hexane afforded 4,6-di-*t*-butyl-3*H*-1,2,3-benzodithiazole 2-oxide (**26**) as white crystals (41 mg). The filtrate was chromatographed (silica gel, hexane). The first fraction gave 15 mg of sulfur. The second fraction gave 24 mg of **4b**. The other fraction, on treatment with CCl_4 followed by filtration, gave 25 mg of **26** as white crystals, and the filtrate was chromatographed (silica gel, CCl_4). A slightly pale yellow fraction gave 133 mg (34.2%) of 2,4,6-tri-*t*-butylaniline (**27**) (identified by IR and NMR). The subsequent fraction gave 95 mg of yellow tar, which, on treatment with hexane, gave 21 mg of **26**. Thus, the total yield of **26** was 87 mg (20.6%); **26**: mp 160 °C (dec) (recrystallized four times from aq methanol); IR (KBr): 3280 (NH) and 1110 cm^{-1} (SO); NMR (CCl_4): δ 1.34 (s, 9H), 1.45 (s, 9H), 7.21 (ABq, J=1.2 Hz, $\Delta\delta$=0.12, 2H), and 7.50 (broad s); $\lambda_{\max}^{\text{hexane}}$ (ε): 284 sh (2130) and 294 sh nm (1560); *m/e*: 283 (M^+, 15%), 268 (23), 266 (100), 251 (39), 236 (15), 57 (21), and 41 (16); mol wt (vapor pressure osmometry, in benzene at 39.8 °C): 293.3 (calcd: 283.43). Found: C, 59.38; H, 7.69; N, 4.90; S, 22.21%. Calcd for $C_{14}H_{21}NOS_2$: C, 59.33; H, 7.47; N, 4.94; S, 22.62%.

*Thermolysis of **4b** in the Presence of* p*-Toluenesulfonic Acid.* A mixture of **4b** (303 mg, 0.94 mmol), *p*-toluenesulfonic acid (14 mg, 0.08 mmol), ethanol (2 ml), and benzene (20 ml) was refluxed for 3 h. Removal of the solvent followed by treatment with hexane afforded 73 mg (27.5%) of **26** as white crystals. The hexane-soluble part was chromatographed (silica gel, hexane) to give 89 mg (29.4% recovery) of **4b** and 97 mg (39.6%) of **27**.

*Thermolysis of **4b** under a Stream of Oxygen.* In refluxing benzene (20 ml), 302 mg (0.93 mmol) of **4b** was heated for 5 h under a stream of oxygen. After the solvent was removed, the residue was treated with hexane; no precipitates (**26**) were obtained. Chromatography (silica gel, CCl_4) of the residue afforded 29 mg (9.5%) of 2-amino-3,5-di-*t*-butylphenyl *t*-butyl disulfide (**32**) as a yellow tarry material, which was identified by the following spectral data: IR (neat): 3495 and 3360 cm^{-1} (NH_2); NMR (CCl_4): δ 1.27 (s, 9H), 1.35 (s, 9H), 1.43 (s, 9H), 4.45 (broad s, 2H), and 7.21 (ABq, J=2.4 Hz, $\Delta\delta$=0.08, 2H); *m/e* 325 (M^+, 2%), 293 (3), 269 (7), 254 (5), 237 (19), 236 (12), 222 (51), and 57 (100).

A crystalline material (176 mg) obtained from the second fraction was subjected to preparative TLC (silica gel, CCl_4) to give 28 mg (11.5%) of **27** and 27 mg (12.2%) of bis(2-amino-3,5-di-*t*-butylphenyl) disulfide (**28**). These compounds were identified by comparison of the IR and NMR spectra with those of the authentic samples. Spectral and analytical data of **28** were listed in the description of hydrolysis of **26** (*vide infra*).

*Hydrolysis of 4,6-Di-*t*-butyl-3*H*-1,2,3-benzodithiole 2-Oxide (**26**).* A solution of **26** (57 mg, 0.2 mmol), potassium hydroxide (189 mg, 3.37 mmol), water (2 ml), and ethanol (7 ml) was refluxed for 2 h. The reaction mixture was neutralized by dil. HCl, and extracted with ether. The extract was washed with aq. sodium hydrogencarbonate, then with water, and dried ($MgSO_4$). After the solvent was removed, the residue was purified by preparative TLC (silica gel, CCl_4) to give 46 mg (97%) of **28** as pale yellow needles (mp 87.7—89.7 °C), which were recrystallized three times from methanol: IR (KBr): 3490 and 3370 cm^{-1} (NH_2); NMR (CCl_4): δ 1.19 (s, 18H), 1.40 (s, 18H), 4.45 (broad s, 4H), and 7.10 (ABq, $\Delta\delta$=0.08, J=2.5 Hz, 4H); *m/e*: 472 (M^+, 21%), 236 (100), 222 (48), 206 (10), 179 (10), 57 (36), and 41 (16). Found: C, 71.22; H, 9.59; N, 6.12; S, 13.67%. Calcd for $C_{28}H_{44}N_2S_2$: C, 71.13; H, 9.38; N, 5.93; S, 13.56%.

ESR Measurements. An ESR sample tube containing *ca.* 0.2 ml of benzene solution (0.05 M) was degassed by four freeze-pump-thaw cycles and heated for 5 min at 110 °C. After the sample solution was cooled to room temperature, the ESR spectra were recorded. Hyperfine splitting constants and *g*-values were determined on the base of Mn^{2+} in MnO_2.

*Photolysis of 2,4-Di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**1**).* Typical procedures are described below. a) A pentane solution (70 ml) of **1** (329 mg, 1.17 mmol) was irradiated for 32.3 h with Pyrex-filtered light from a 100 W medium pressure mercury lamp immersed in the solution, whose temperature was controlled by external cooling with ice-water not to exceed 25 °C. After removal of the solvent, the residue was subjected to DCC (silica gel, hexane). The first fraction gave 12 mg (16%) of sulfur. An orange fraction gave 193 mg (70.9%) of **17** as orange crystals, which were recrystallized four times from aq ethanol and once from acetone; mp 122—123 °C; IR (KBr): 2950, 1360, 1280, 1265, and 1238 cm^{-1}; NMR (CCl_4): δ 1.29 (s, 36H), 2.24 (s, 6H), 6.91 (d, $J=2$ Hz, 2H), and 7.17 (d, $J=2$ Hz, 2H); λ_{max}^{hexane} (ε): 317 (5530) and 409 nm (6560); *m/e* 466 (M^+, 0.5%), 451 (7), 247 (13), 232 (47), 219 (37), 204 (100), 57 (27), and 41 (23). Found: C, 77.05; H, 10.12; N, 5.86; S, 6.94%. Calcd for $C_{30}H_{46}N_2S$: C, 77.20; H, 9.93; N, 6.00; S, 6.87%.

The last fraction gave 83 mg of tarry metarial, which was purified by TLC (silica gel, benzene) to give 68 mg (26.5%) of 2,4-di-*t*-butyl-6-methylaniline (**7**).

b) Effect of Concentration. A solution of **1** in pentane (1.5 ml) was placed in a quartz tube, flashed with nitrogen, immersed in a water bath to keep the temperature of the solution below 20 °C, and irradiated with Pyrex-filtered light from a 400 W medium pressure mercury lamp. In this way, several solutions were irradiated at the same time. Determination of molar ratios (**7**/**17**) was performed by high speed liquid chromatography (1-m column packed with Hitachi 3010 gel, eluted with methanol). The results were shown in Table 3.

*Photolysis of **1** in EPA Matrix.* An EPA solution in a Pyrex cell was degassed by four freeze-pump-thaw cycles. This sample solution was immersed in liquid nitrogen in a Dewar vessel made of quartz which was placed in a Cary-14 spectrophotometer, and irradiated by focused light from a medium pressure mercury lamp through the Dewar vessel. Electronic spectra were recorded intermittently.

N,N′-*Bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur Diimide (**17**).* A pentane solution (70 ml) of **17** (187 mg, 0.40 mmol) was irradiated for 33 h with a 100 W medium pressure mercury lamp immersed in the solution, whose temperature was controlled not to exceed 15 °C. The irradiated solution was examined by high speed liquid chromatography (column material: Hitachi 3010; column length: 1 m; column pressure: 45 kg/cm^2; flow rate: 1.2 ml/min; solvent: methanol) and found to show three peaks: corresponding to **7**, an unknown compound which did not correspond to **6**, and **17**. Molar ratio **7**/**17** was estimated to be 0.215. The reaction mixture was subjected to preparative TLC (silica gel, hexane, developed three times) to give 128 mg (68.3% recovery) of **17** and 28 mg of brown tarry material, which was purified by TLC (silica gel, benzene) to give 16 mg (18.2%) of **7**.

*Photolysis of **4b**.* A pentane solution (70 ml) of **4b** (402 mg, 1.24 mmol) was irradiated by Pyrex-filtered light from a 100 W medium pressure mercury lamp for 32.8 h. Temperature of the solution was controlled not to exceed 20 °C by cooling with ice-water. After removal of the solvent, the residue which was composed of many components was subjected to DCC (silica gel, hexane). From an orange fraction was obtained 38 mg of orange crystalline material, which was recrystallized from acetone to give 26 mg (7.5%) of *N*,*N*′-bis(2,4,6-tri-*t*-butylphenyl)sulfur diimide (**43**) (identified by comparison of the spectral data with those of an authentic sample).[1] From a pale yellow fraction, 35 mg (10.6%) of aniline (**27**) was obtained.

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