Spectroscopic Detection and Reactions of a Thionitroso Compound

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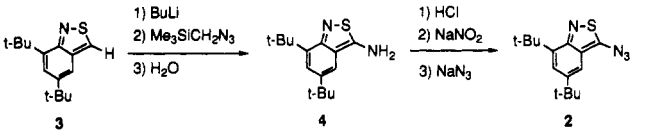
Abstract: 2,4-Di-*tert*-butyl-6-cyanothionitrosobenzene (**1**) was generated by the photochemical and thermal reactions of 7-azido-2,4-di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (**2**) and detected by means of UV-vis and infrared spectra in matrices at cryogenic temperatures. Various reactions of **1**, such as [2+3] and [2+4] cycloadditions, oxidation, reduction, and sulfurization, were investigated. Some of these reactions represent novel reactivities of a thionitroso compound.

Organic compounds containing multiple bonds between the second- and higher-row elements are of current interest, and a number of new compounds of this type have been synthesized in recent years.[2] As for compounds of the double bond containing sulfur, thiocarbonyl compounds have been widely studied and applied in organic synthesis.[3] As for compounds having N=S bonds, however, only some scattered examples of thionitroso compounds (RN=S) have been studied,[4-16] although RN=S=X type of thiocumulenes have been extensively studied.[17]

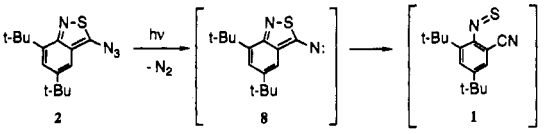
N,N-Dimethylthionitrosoamine was reported by Middleton as a rather unstable but isolable compound,[4] but it is considered to be electronically stabilized by the strong mesomeric effect of the dimethylamino group and hence the nature of N=S bond is substantially changed. No stable *C*-thionitroso compound has yet been isolated so far. *C*-Thionitroso compounds have been re-

Scheme I



3 4 2

Scheme II



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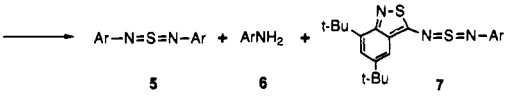

5 6 7

[Ar = 2,4-di-t-butyl-6-cyanophenyl]

Table I. Products of Photoreaction of Azidoisothiazole **2**

entry	solvent	temp/°C	products/% 5	6	7
1	hexane	0	78	16	2
2	THF	0	76	14	2
3	THF + H_2O[a]	0	59	14	5
4	EPA[b]	0	46	51	trace
5	ethanol	0	5	91	3
6	isopentane[c]	-78	76	13	3
7	MTHF[d]	-78	63	30	2
8	EPA[b]	-78	62	19	2
9	ethanol	-78	43	33	8

[a] 5 vol % of water was added to THF. [b] Ether:isopentane:ethanol = 5:5:2. [c] Isopentane + pentane (2 vol %). [d] 2-Methyltetrahydrofuran.

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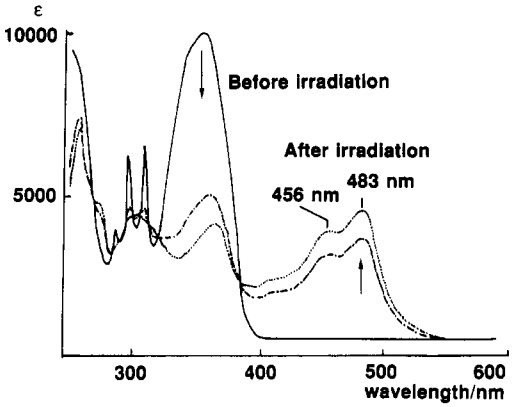


Figure 1. Photolysis of azidoisothiazole **2** in argon matrix (12 K) monitored by electronic spectroscopy.

portedly trapped only in Diels–Alder reaction, ene reaction, and dimerization.

The purpose of this paper is to study the spectroscopic detection of thionitrosoarene **1** generated from the photochemical ring-opening reaction of azidobenzisothiazole **2** using a matrix isolation technique and to reveal some new reactivities of the thionitrosoarene **1**.

Results and Discussion

Preparation and Photochemical Reaction of Azidoisothiazole 2. In this study we used a photochemical ring opening of an azidobenzisothiazole reported by Joucla and Rees[12] for the generation of a thionitroso intermediate. Azidobenzisothiazole **2** having an ortho *tert*-butyl group was chosen as a precursor, since the bulky *tert*-butyl group is expected to kinetically stabilize a thionitroso compound. **2** was prepared as shown in Scheme I. 2,4-Di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (**3**)[13] was lithiated by butyllithium and then aminated with (trimethylsilyl)methyl azide[19] to give 7-amino-2,4-di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (**4**) in 40% yield. **2** was prepared in 54% yield via diazotization of **4** followed by substitution reaction with sodium azide.

The irradiation of **2** in organic solvents with a medium-pressure mercury lamp afforded *N*,*N*′-bis(2,4-di-*tert*-butyl-6-cyanophenyl)sulfur diimide (**5**), 2,4-di-*tert*-butyl-6-cyanoaniline (**6**), and *N*-(2,4-di-*tert*-butyl-6-cyanophenyl)-*N*′-(2′,4′-di-*tert*-butyl-8′,9′-thiazabicyclo[4.3.0]nona-2′,4′,6′,9′-tetraen-7′-yl)sulfur diimide (**7**) (Scheme II; Ar denotes 2,4-di-*tert*-butyl-6-cyanophenyl hereafter). The reaction conditions and the yields of these products are summarized in Table I. The results in Table I show a remarkable solvent effect in the photochemical reaction of **2** at 0 °C in ethanol-containing media, but the effect diminished in the reaction at −78 °C. This fact suggests that essentially the same reaction occurred in each solvent at very low temperature. In view of the results by Joucla and Rees,[12] the formation of sulfur diimide **5** is suggestive of involvement of a thionitroso intermediate also in this reaction.

The most plausible mechanism of the photoreaction is shown in Scheme II. The starting azide **2** loses molecular nitrogen to give a nitrene intermedite **8**, which undergoes the ring-opening reaction to produce a thionitroso intermediate **1**. The thionitroso intermediate **1** affords sulfur diimide **5** by dimerization and subsequent desulfurization, aniline **6** by reaction with solvent, and unsymmetrical sulfur diimide **7** by 1,3-dipolar cycloaddition reaction with starting azide **2** followed by a loss of molecular nitrogen. The details of the formation mechanism of **6** and **7** will be discussed later.

Spectroscopic Detection of Thionitrosoarene 1. For the purpose of detecting an intermediate in the photoreaction of **2**, the reaction was carried out in matrices at cryogenic temperatures and monitored by UV–vis and IR spectra. When **2** was irradiated in an argon matrix at 12 K and the reaction was monitored by electronic spectroscopy, new absorption bands at 456 and 483 nm appeared at the expense of the absorption of the starting azide at 354 nm as shown in Figure 1. The change of the electronic spectra had isosbestic points, which demonstrated the generation of a single product during the irradiation at this temperature. Since this spectrum was different from those of any reaction products, the intermediate is considered to be nitrene **8** or thionitroso compound **1**.

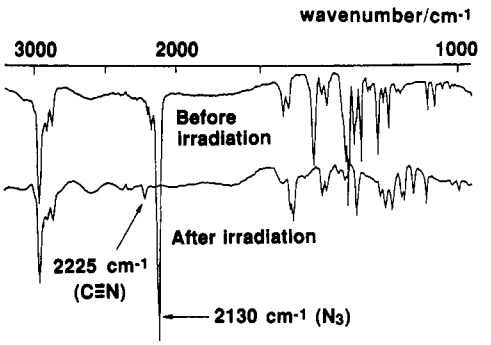
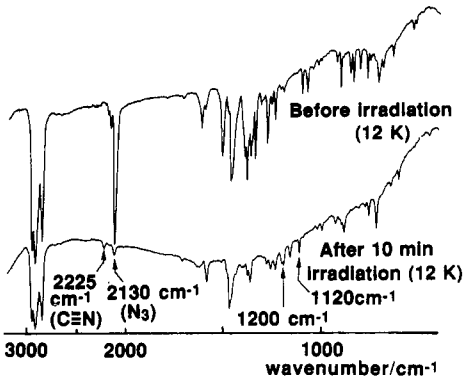


Figure 2. Photolysis of azidoisothiazole **2** in argon matrix (12 K) monitored by IR spectroscopy.



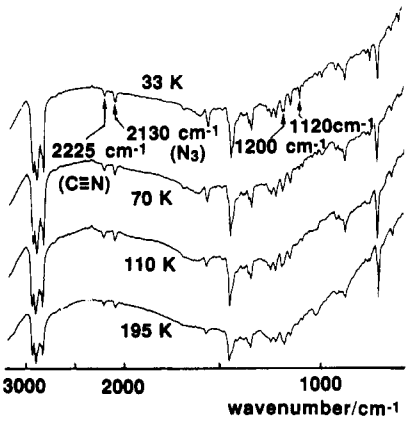


Figure 3. Photolysis of azidoisothiazole **2** in undecane matrix (12 K) monitored by IR spectroscopy: (a, top) change during irradiation; (b, bottom) change during warming after irradiation.

When **2** was irradiated at 12 K in a similar argon matrix and the reaction was monitored by IR spectroscopy, the absorption band due to a cyano group (2225 cm^{-1}) appeared gradually at the expense of the absorption due to the azide group (2130 cm^{-1}) (Figure 2). Since the formation of a cyano group is diagnostic of the formation of the thionitroso compound **1** as shown in Scheme II, the intermediate observed during the irradiation of **2** at 12 K is not nitrene **8** but thionitroso compound **1**.

When **2** was irradiated in an undecane matrix at 12 K (Figure 3), the absorption due to a cyano group appeared at 2225 cm^{-1} as observed in the photolysis of **2** in argon matrix. When the sample was warmed to 70 K after the irradiation was over, the

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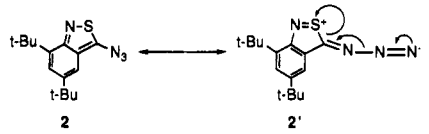
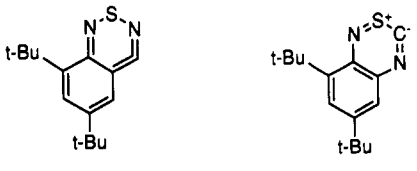
Scheme III



absorptions at 1200 and 1120 cm^{-1} began to decrease and they disappeared completely at 110 K. Schmidt et al. have reported that the calculated (SCF/3-21G) stretching frequency of N=S bond in HN=S is 1245 cm^{-1}.[20] Since it is known that the experimental value of the stretching frequency can be estimated by multiplying the calculated value by 0.9, the experimental stretching frequency of HN=S is estimated to be about 1100 cm^{-1}. Although the exact assignment of the N=S stretching of thionitrosoarene **1** is difficult because of the complexity of the IR spectra, the absorption at 1120 or 1200 cm^{-1} is reasonably assigned to the N=S stretching of **1**.

The position and intensity of the absorption maxima in the UV–vis spectra (456 and 483 nm, ϵ = 4000 and 4600) of **1** are similar to those of 2-nitrosothionitrosobenzene (485 nm, ϵ = 8000–9000) reported by Pedersen in the photolysis of benzo-[*c*]-1,2,5-thiadiazole 2-oxide.[11] This fact suggests that Pedersen probably observed the thionitroso intermediate. The assignment is also compatible with the fact that the compounds having N=S=S or N=S=N chromophores have absorption bands in a similar region (ArN=S=S λ_{max} = 465 nm in isopentane, Ar-N=S=NAr λ_{max} = 431 nm in EPA; Ar = 2,4-di-*tert*-butyl-6-cyanophenyl). Mayer et al. reported that the calculated absorption maxima of thionitrosobenzene are 303, 323 nm (π–π^*, by PPP), 491, and 1234 nm (n–π^*, by CNDO/S).[18] Although the observed value of 483 nm is rather close to the calculated value of 491 nm, the intensity of the observed absorption (ϵ = 4500) indicates that the absorption band around 483 nm should be assigned to π–π^* transition. The results obtained in the present study and those by Pedersen suggest that more sophisticated calculations are necessary for the electronic spectrum of thionitrosobenzene.

Direct formation of thionitroso compound **1** instead of nitrene **8** even at 12 K is probably due to the special structure of **2** where the importance of the canonical structure **2'** (Scheme III) permits the simultaneous loss of nitrogen and ring opening. However, the possibility of involvement of a singlet nitrene **8** with a very short lifetime cannot be rigorously excluded. Although the structures of the ring-expanded products **1'** and **1''** might be considered instead of **1** in view of the known formation of azacycloheptatriene in the photochemical reaction of phenyl azide,[21] they can be excluded because of the absence of a cyano group in **1'** and **1''** and the lack of isonitrile derivatives in the products.



1' **1''**

Since the Mayer's calculation (STO-3-21G)[18] suggests that a thionitroso compound, HN=S, may exist as a ground-state triplet molecule, an ESR study was also performed for the present photoreaction. Although the photoreaction of **2** was carried out in various organic glasses such as EPA, 2-methyltetrahydrofuran, or methylcyclohexane at cryogenic temperature, neither the ESR signal of nitrene intermediate **8** nor that of thionitrosoarene **1** was observed. This result is consistent with the conclusion based on the aforementioned electronic and IR experiments that thionitrosoarene **1** is generated directly from azidoisothiazole **2** or the lifetime of **8** is too short to be detected spectroscopically. Since the triplet signal of thionitrosoarene **1** could not be detected in this ESR study, thionitrosoarene **1** is not considered to exist as triplet ground state. The present result is consistent with the Mayer's calculation that the lowest triplet state lies slightly higher than the singlet ground state in the case of thionitrosobenzene.[18]

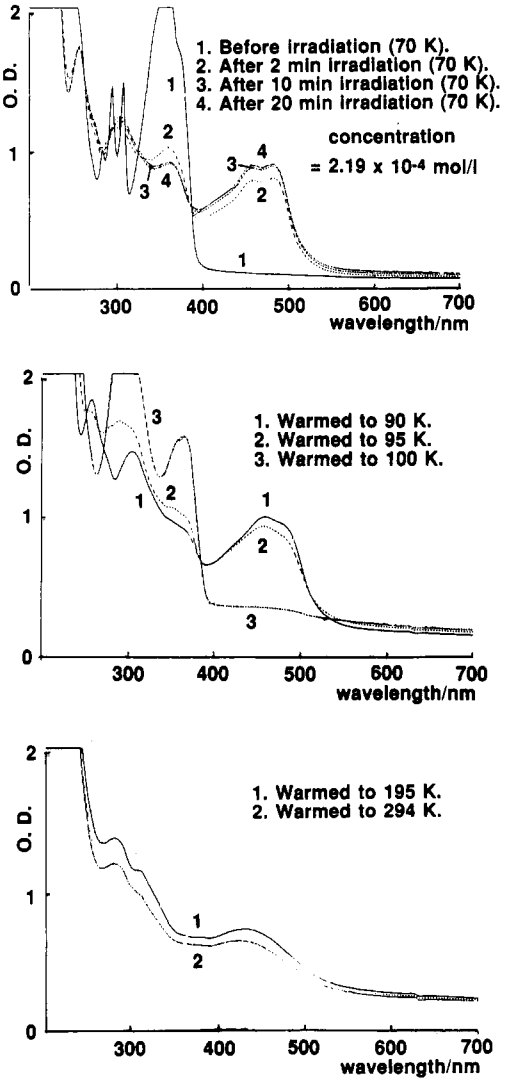


Figure 4. Photolysis of azidoisothiazole **2** in EPA matrix (12 K) monitored by electronic spectroscopy: (a, top) change during irradiation; (b, center) change during warming after irradiation (90–100 K); (c, bottom) change during warming after irradiation (195–294 K).

Photoreaction of Azidoisothiazole 2 in Organic Glasses. In order to obtain information on the stability of thionitrosoarene **1** and the details of the photoreaction of azidoisothiazole **2**, photolysis of **2** was carried out in various organic glass matrices and monitored by UV–vis spectroscopy.

When **2** was irradiated at 70 K in an EPA matrix and the reaction was monitored by electronic spectroscopy, a spectrum with the absorption maxima at 460 and 484 nm appeared at the expense of the absorption of the starting azide (Figure 4). Since the spectrum was similar to that observed in the experiment in argon matrix, the intermediate can be assigned to thionitrosoarene **1**. After irradiation, the sample was warmed gradually to room temperature. The initially observed spectrum at 70 K did not change significantly up to 90 K. At 100 K a remarkable change was observed; the absorption band longer than 400 nm disappeared and new absorption bands (λ_{max} = 287, 304, 365 nm) appeared. Those absorptions disappeared at 170 K (after the melting of EPA matrix) and instead appeared the absorption with maxima at 426 nm which is assignable to the absorption of sulfur diimide **5**. The yield of **5** calculated from the absorption coefficient was 64%. The

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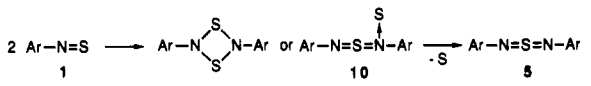
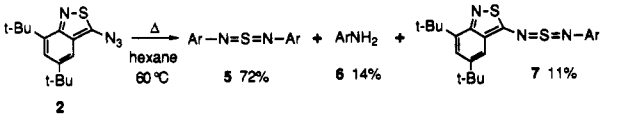
Scheme IV



Scheme V



temperature (100 K) where the change was observed in the UV–vis spectra roughly corresponds to that of disappearance of the absorption at 1200 and 1120 cm^{-1} in the IR spectra mentioned above. Considering the mechanism of the photoreaction of **2**, the change in the electronic spectra at 100 K is most reasonably regarded as dimerization of thionitrosoarene **1** (Scheme IV).

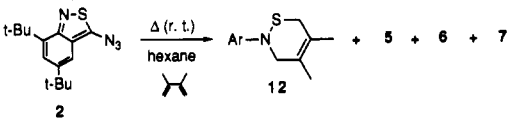
This interpretation is supported by a relationship between the viscosity of matrices and the disappearance temperature of thionitrosoarene **1**. The spectrum of **1** disappeared at ca. 100 K in rigid matrices such as EPA ($\eta = 5.5 \times 10^{-2}$; η = viscosity relative to 3-methylpentane at 77 K)[22] or 3-methylpentane (η = 1), while that disappeared at 72 K in soft matrices such as isopentane (isopentane:3-methylpentane = 9:1; $\eta = 3.8 \times 10^{-6}$). These results indicate that the softer the organic glasses the lower the disappearance temperature of the thionitroso intermediate which undergoes dimerization. A similar relation between the viscosity of matrices and the reaction rates was observed in the dimerization reaction of silylenes to a disilene.[23]

A possible structure of the dimer of thionitrosoarene **1** is either dithiadiazetidine **9** or sulfur diimide *N*-sulfide **10**. Since **9** has no heteroatom-conjugated chromophore, it should not have the absorption band in the visible region in view of the absorption maxima of aniline **6** at 326 nm (in EPA) and of *N*,*N*′-bis(2,4-di-*tert*-butyl-6-cyanophenyl)diaminosulfur (ArNHSNHAr) (**11**) at 319 nm (in EPA). Conversely, **10** has an N=S=N chromophore and the absorption might appear in the visible region. It seems reasonable that coordination of sulfur to the nitrogen in sulfur diimide **5** shifts the absorption of 431 nm (in EPA) to 365 nm considering the fact that the absorption band of azo compounds undergoes a hypsochromic shift by about 100 nm on going to the corresponding azoxy compounds.[24] Therefore, the structure of the dimer of thionitrosoarene **1** can be assigned to sulfur diimide *N*-sulfide **10**.

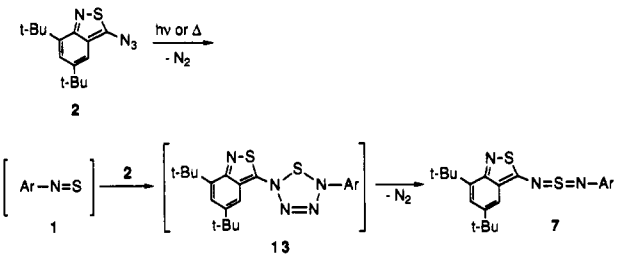
Reactions of Thionitrosoarene 1. Thionitrosoarene **1** was generated in situ by the photochemical and thermal reactions of azidoisothiazole **2**, and its reactions were investigated in the presence of various reagents.

Thermal reactions of azidoisothiazole **2** in hexane afforded the same products as those in the photoreaction. Namely, the reaction at 60 °C for 1 h afforded 72% of sulfur diimide **5**, 14% of aniline **6**, and 11% of unsymmetrical sulfur diimide **7** (Scheme V). The thermal reaction slowly proceeded also at room temperature to give **5** (50%), **6** (40%), and **7** (7%). The similarity of the products to those in the photoreaction indicates that the thermal reaction also proceeds through the intermediacy of **1**. When the thermal reaction of **2** was carried out in ethanol at 60 °C, **5**–**7** were obtained (18, 68, and 10%, respectively). **5** was confirmed to be stable in ethanol under the photochemical and thermal reaction conditions. A relatively high yield of **6** in ethanol is considered to result from the facile addition of ethanol to thionitrosoarene **1** followed by hydrolysis. In light of the fact that aniline **6** was formed also in hydrocarbon solvents, aniline **6** is considered to be formed also by hydrogen abstraction of **1** and subsequent loss of sulfur. As mentioned above, theoretical calculations on HN=S have shown that the energy gap between its ground singlet state and lowest triplet state is very small,[18] suggesting the possibility that the thionitroso group has some biradical character and is able to abstract hydrogen atom from solvents. In the thermal and photochemical reactions of **2** in alcoholic solvents, the above two pathways to aniline **6** may both be operative.

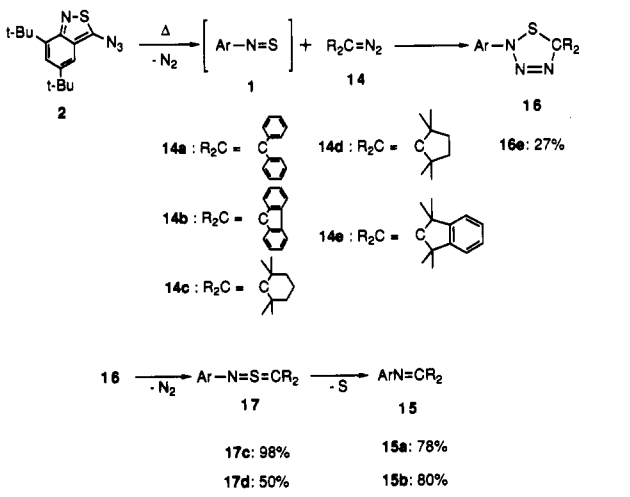
Scheme VI



Scheme VII



Scheme VIII



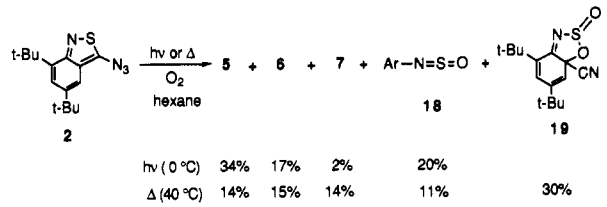
(a) [2+4] Cycloaddition Reactions. Since thionitroso intermediates are known to react with dienes to give Diels–Alder adducts,[5-7,10,12,16] **1** is expected to undergo [2+4] cycloaddition reactions. Indeed, the [2+4] adduct **12** was isolated in 14% yield in the thermal reaction of azidoisothiazole **2** in hexane at room temperature for 3 days in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (Scheme VI). Although cyclic dienes are expected to have higher Diels–Alder reactivities than the acyclic diene, neither cyclopentadiene, furan, nor anthracene afforded the [2+4] adduct of **1**. The thermal reaction of **2** in the presence of those cyclic dienes resulted in the formation of only **5**–**7**. It seems that the steric bulkiness of **1** prevents the reaction with the cyclic dienes or that the steric crowdedness of Diels–Alder adducts of **1** with the cyclic dienes permits the retro-Diels–Alder reaction under the reaction conditions to regenerate the thionitroso intermediate **1**.

(b) [2+3] Cycloaddition Reactions. The unsymmetrical sulfur diimide **7** was produced in both the thermal and photochemical reactions of azidoisothiazole **2**. The most plausible mechanism for the formation of **7** is the 1,3-dipolar cycloaddition reaction of **1** with azide **2** followed by loss of nitrogen from an unstable thiatetrazoline intermediate **13** (Scheme VII). This result suggests the possibility of [2+3] cycloaddition reactivity of thionitrosoarene **1**.

Although a similar cycloaddition reaction can be expected to occur in the thermal reaction of **2** in the presence of other aromatic

(22) *Handbook of Photochemistry*; Murov, S. L. Ed.; Marcel Dekker: New York, 1973; pp 90–93.
(23) Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, 209.
(24) *Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds*; Hirayama, K., Ed.; Plenum Press Data Division: New York, 1967; pp 128, 141.

Scheme IX



azides, the thermal reaction in the presence of aryl azides such as phenyl, *p*-chlorophenyl, and *p*-methylphenyl azides at room temperature for 3 days did not afford the expected unsymmetrical sulfur diimides. 1,3-Dipolar cycloaddition of **1** with **2** seems to proceed because of the high reactivity of **2** which comes from the large contribution of a canonical structure **2'** increasing the electron density on the azide group.

Diazo compounds having higher 1,3-dipolar reactivity than aryl azides reacted with **1** (Scheme VIII). When **2** was allowed to react with an excess (4 equiv) of diphenyldiazomethane (**14a**) and 9-diazofluorene (**14b**) in hexane at room temperature, imines **15a** and **15b** were obtained in 78 and 80% yields, respectively.

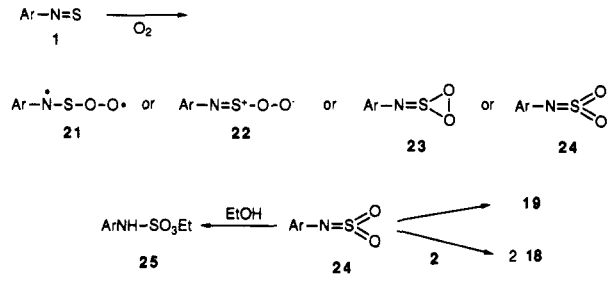
The formation of the imines can be explained as follows. The diazo compounds undergo 1,3-dipolar cycloaddition with **1** to give thiatriazoline intermediates **16a,b**, which lose nitrogen to give thiocarbonylimines **17a,b** and then desulfurize to afford imines **15a** and **15b**. Indeed, when the thermal reaction of **2** was carried out with an excess amount of diazo compounds having bulky alkyl groups like 2,2,6,6-tetramethyldiazocyclohexane (**14c**) and 2,2,5,5-tetramethyldiazocyclopentane (**14d**) in hexane at room temperature, thiocarbonylimines **17c** (98%) and **17d** (50%) were isolated, respectively. The structures of **17c,d** were established on the basis of ^{13}C NMR (*C*=S=N at δ 180–190), IR (ν_{max} 960 cm^{-1} (C=S=N)), and UV–vis (λ_{max} 400 nm) spectra.[17c] Thiocarbonylimines are known to desulfurize via a thiazine intermediate to give imines.[17c] The difference between the products from **14a,b** and **14c,d** is probably due to the difference in the stability of intermediary thiocarbonylimines, which are stabilized by the bulky alkyl groups in the cases of **17c,d**. It is also notable that a similar thermal reaction of **2** in the presence of 2-diazo-1,1,3,3-tetramethylindan (**14e**) afforded 2-(2',4'-di-*tert*-butyl-6'-cyanophenyl)-5-(1'',1'',3'',3''-tetramethyl-2''-indenylidene)-1,2,3,4-thiatriazoline (**16e**) (32%), a new type of five-membered heterocycle. These results support the mechanism shown in Scheme VIII. These reactions represent the first example of [2+3] cycloaddition of thionitroso compounds and a new mode of preparation of thiocarbonylimines as well.

The reactions of **1** with other 1,3-dipoles such as mesitonitrile oxide or *N*-α-diphenylnitrone did not give [2+3] cycloadducts.

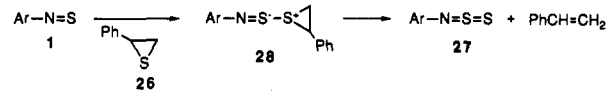
(c) Reaction with Molecular Oxygen. Thionitrosoarene **1** also reacted with molecular oxygen. When **2** was irradiated in hexane at 0 °C with oxygen being bubbled, 2,4-di-*tert*-butyl-6-cyano-*N*-sulfinylaniline (**18**) (20%) was obtained in addition to **5** (34%), **6** (17%), and **7** (2%). The thermal reaction of **2** in hexane at 40 °C with oxygen afforded **18** (11%) and 2,4-di-*tert*-butyl-6-cyano-7,8,9-oxathiazabicyclo[4.3.0]nona-2,4,9-triene (**19**) (30%) in addition to **5** (14%), **6** (15%), and **7** (14%) (Scheme IX).

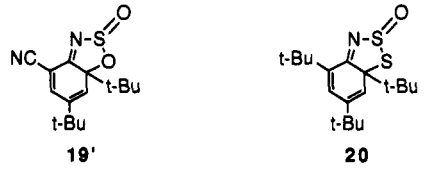
The structure of **19** was confirmed by elemental analysis and spectroscopic data. **19** showed an AX signal of olefinic protons at δ 5.99 and 6.60 in ^1H NMR and signals of the aliphatic quaternary carbon attached to the nitrile group at δ 87.6 and the nitrile carbon at δ 113.7 in ^{13}C NMR. Although the absorption due to CN stretching was not observed in the IR spectrum, it is well documented that the introduction of an oxygenated group into the molecule results in a "quenching" of the CN absorption intensity to a remarkable extent, and its effect is greater when the oxygen-containing group is attached to the same carbon atom as the nitrile.[25] Furthermore, the UV spectrum of **19** (λ_{max} 345 nm, ϵ 1500 in hexane) bears a close resemblance to that of **20** (λ_{max} 345 nm, ϵ 2930 in hexane), whose structure was established by X-ray crystallography,[26] supporting similarity in structure between **19** and **20**. Although the structure **19'** cannot be rigorously excluded for **19**, we think that **19** is more likely for steric reasons.

Scheme X



Scheme XI





The formation of **18** and **19** in the above reaction can reasonably be interpreted in terms of intermediacy of **1** as shown in Scheme X. It is notable that thionitrosoarene **1**, which is considered to be a ground-state singlet as mentioned by ESR experiments, reacts with triplet molecular oxygen in both photochemical and thermal reactions of **2**, in contrast to nitrosoarenes which are stable to molecular oxygen, and resembles triplet phenylnitrene which reacts readily with molecular oxygen to form nitrosobenzene oxide.[27] Although it is not certain whether the direct precursor of **19** is any of **21**–**24**, we think that the formation of **19** is best explained by the intramolecular cycloaddition of **24**, since we previously found a similar type of intramolecular cycloaddition for *N*-thiosulfinylanilines.[28] The fact that an ethanol adduct (**25**) of **24** was obtained when **2** was kept in ethanol at 40 °C for 3 h with oxygen being bubbled strongly suggests the intermediacy of the sulfonylaniline **24**. The formation of *N*-(2,4-di-*tert*-butyl-6-cyanophenyl)sulfamate (**25**) by ethanolysis of **19** can be eliminated by the fact that **19** was stable toward ethanol under similar reaction conditions. The cyclization of **24** can be regarded as 1,5-dipolar cyclization or intramolecular 1,3-dipolar cycloaddition as in the case of intramolecular cyclization of *N*-thiosulfinylanilines[28] and represents the first example of 1,3-dipolar behavior of *N*-sulfonylanilines (RN=SO_2). It is noteworthy that **24** undergoes cyclization at the sacrifice of aromatic stabilization.[29]

The absence of the product **19** in the photochemical reaction is considered to be due to photochemical instability of **19**.

The oxidation reaction mentioned above obviously indicates the higher reactivity of a thionitrosoarene than a thiocarbonyl compound. In the case of thiocarbonyl compounds, an oxidation reaction of a thione to a thione *S*-oxide (R_2C=S=O) does not proceed generally with molecular oxygen and needs a stronger oxidating reagent such as a peracid[30] although thiobenzophenone

(25) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, 2nd ed.; Willy: New York, 1964; p 266.

(26) Inagaki, Y.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3615.

(27) (a) Sawaki, Y.; Ishikawa, S.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 584. (b) Ishikawa, S.; Tsuji, S.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 4282.

(28) (a) Inagaki, Y.; Okazaki, R.; Inamoto, N. *Tetrahedron Lett.* **1975**, 4575. (b) Okazaki, R.; Inoue, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3541.

(29) For other reactivities of *N*-sulfonylanilines, see: (a) Quast, H.; Kees, F. *Chem. Ber.* **1981**, *114*, 774. (b) Agawa, T.; Ohshiro, Y. *Yuki Gosei Kagaku Kyokai Shi* **1975**, *33*, 679.

(30) Schönberg, A.; Mostafa, A. *J. Chem. Soc.* **1943**, 275.

is known to react rather slowly with molecular oxygen.[31]

(d) Sulfurization Reaction. The thermal reaction of **1** with phenylthiirane (**26**) in hexane at 30 °C afforded 2,4-di-*tert*-butyl-6-cyano-*N*-thiosulfinylaniline (**27**) (31%) along with **5** (13%), **6** (13%), and **7** (5%). The reaction most likely proceeds via an ylide **28** (Scheme XI). **28** is thought to be formed from the nucleophilic attack of thiirane **26** on the sulfur atom of **1**, since the thionitroso compounds (RN=S) are considered to be polarized like $N^{\delta-}=S^{\delta+}$ by theoretical calculation.[18]

The reaction of **1** with **26** is similar to that of thiobenzophenone, which reportedly gives a transient thione *S*-sulfide $Ph_2C=S=S$,[32] although the reactivity of **1** is definitely much higher than that of the thioketone if one considers the lower concentration of the transient species **1**.

Experimental Section

General Procedures. All the melting points were uncorrected. All the solvents used in the reactions were purified by the reported methods. THF and ether were purified by distillation from benzophenone ketyl before use. All the reactions were carried out under argon atmosphere unless otherwise noted. Preparative liquid chromatography was performed by LC-08 with a JAI gel 1H column (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography was performed with ISN silica DCC 60A. For flash column chromatography Merck Kieselgel 60 Art. 9385 was used. Preparative thin-layer chromatography was done with Merck Kieselgel 60 PF254 Art. 7747.

The UV–vis spectra were recorded with Hitachi-340 and Jasco UVDEC-610 spectrophotometers, and the IR spectra were recorded with Hitachi 260-30 and Hitachi 270-30 spectrophotometers. The ^1H NMR spectra were measured in $CDCl_3$ with JEOL FX-90Q (90 MHz), JEOL GSX-400 (400 MHz), and Brucker AM-500 (500 MHz) spectrometers using $(CH_3)_4Si$ as an internal standard. The ^{13}C NMR spectra were measured in $CDCl_3$ with a JEOL FX-90Q (22.5 MHz), JEOL GSX-400 (100 MHz), and Brucker AM-500 (125 MHz) spectrometers using $(CH_3)_4Si$ as an internal standard. Mass and high-resolution mass spectra were recorded with a JEOL JMS-D300 mass spectrometer. A Varian E112-V7800 X-band spectrometer (9.30 GHz) was used for recording the ESR spectra.

Preparation of 7-Amino-2,4-di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (4). A hexane solution of butyllithium (1.75 M) (14.5 mmol) was added to a THF solution (60 mL) of 2,4-di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (**3**)[13] (3.00 g, 12.1 mmol) and hexamethylphosphoric triamide (3 mL) at −78 °C. The solution was stirred for 10 min at −78 °C and then for 30 min at 0 °C. A THF solution (30 mL) of (trimethylsilyl)methyl azide[19] (3.60 mL, 24.8 mmol) was added to the solution at −78 °C. After the reaction mixture was stirred for 1 day at room temperature, the reaction was quenched by a saturated aqueous solution of NH_4Cl. The mixture was extracted with ether, and the organic layer was washed with water twice and dried over anhydrous $MgSO_4$. After the removal of the solvent, the resulting mixture was chromatographed (dry column chromatography, silica gel, hexane–ether (2:1)) to afford **3** (first fraction, 0.95 g, 32%) and **4** (second fraction, 1.28 g, 40%). **4** was recrystallized from ethanol to give colorless crystals. **4**: mp 171.0–172.0 °C; ^1H NMR (500 MHz) δ 1.36 (s, 9 H), 1.59 (s, 9 H), 4.81 (bs, 2 H), 7.20 (AB q, 2 H, Δδ = 0.21 ppm, J = 1.86 Hz); ^{13}C NMR (125 MHz) δ 29.7, 31.0, 34.8, 35.9, 110.9, 122.2, 124.0, 142.3, 142.7, 159.3, 167.2; IR (KBr) 3450 ,3350(NH_2) cm^{-1}; MS m/z 262 (M^+, 20%), 247 (50), 230 (36), 215 (86), 57 (100); HRMS 262.1502, calcd for $C_{15}H_{22}N_2S$ 262.1502. Anal. Calcd for $C_{15}H_{22}N_2S$: C, 68.66; H, 8.45; N, 10.67; S, 12.22. Found: C, 68.41; H, 8.27; N, 10.63; S, 12.71.

Preparation of 7-Azido-2,4-di-*tert*-butyl-8,9-thiazabicyclo[4.3.0]nona-2,4,6,9-tetraene (2). Hydrogen chloride gas was bubbled into an ethereal solution (20 mL) of **4** (250 mg, 0.95 mmol) at 0 °C until no more precipitate of the salt of **4** formed. After removal of the excess hydrogen chloride gas and the solvent, the remaining white salt was suspended in 3 M hydrochloric acid (5 mL). To the suspension was added an aqueous solution (2 mL) of sodium nitrite (79 mg, 1.1 mmol), and the solution was stirred for 1 h at 0 °C. An aqueous solution (2 mL) of sodium azide (76 mg, 1.1 mmol) was added to the solution of diazonium salt, and then the reaction mixture was stirred for 10 min at 0 °C. The reaction mixture was extracted with ether and dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was chromatographed (dry column chromatography, silica gel, hexane) to afford **2** (148 mg, 54%). **2** was recrystallized from pentane (−78 °C) to give pale yellow crystals. **2**: mp 77.0–79.0 °C dec; ^1H NMR (400 MHz) δ 1.35 (s, 9 H), 1.59 (s, 9 H), 7.32 (AB q, 2 H, Δδ = 0.08 ppm, J = 1.8 Hz); ^{13}C NMR (100 MHz) δ 29.9, 30.8, 35.0, 36.0, 111.6, 124.6, 127.1, 142.7, 146.1, 157.4, 160.0; IR (KBr) 2120 (N_3) cm^{-1}; UV–vis (hexane) 228 nm (ε 18 400), 255 (sh, 6900), 297 (4300), 312 (4300), 356 (7700); MS m/z 288 (M^+, 8%), 260 (19), 245 (12), 228 (13), 213 (31), 57 (100); HRMS 288.1403, calcd for $C_{15}H_{20}N_4S$ 288.1408. Anal. Calcd for $C_{15}H_{20}N_4S$: C, 62.47; H, 6.99; N, 19.43; S, 11.12. Found: C, 62.42; H, 6.98; N, 19.37; S, 11.16.

Photolysis of 2 in Hexane. A hexane solution (70 mL) of **2** (100 mg, 0.35 mmol) was irradiated by a medium-pressure mercury lamp (100 W) with a Pyrex filter for 45 min at 0 °C under nitrogen. After removal of the solvent, the residue was chromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)). The first fraction gave a deep pink viscous oil of *N*-(2,4-di-*tert*-butyl-6-cyanophenyl)-*N'*-(2',4'-di-*tert*-butyl-8',9'-thiazabicyclo[4.3.0]nona-2',4',6',9'-tetraen-7'-yl)sulfur diimide (**7**) (2 mg, 2%), which was recrystallized from ethanol to afford dark pink crystals. The second fraction gave an orange viscous oil of *N,N'*-bis(2,4-di-*tert*-butyl-6-cyanophenyl)sulfur diimide (**5**) (66 mg, 78%), which was recrystallized from ethanol to afford red crystals. The third fraction gave a colorless viscous oil of 2,4-di-*tert*-butyl-6-cyanoaniline (**6**) (13 mg, 16%), which was recrystallized from ethanol to afford colorless crystals. **5**: mp 175.0–175.5 °C; ^1H NMR (90 MHz) δ 1.29 (s, 18 H), 1.31 (s, 18 H), 7.59 (AB q, 2 H, Δδ = 0.15 ppm, J = 2.20 Hz); ^{13}C NMR (22.5 MHz) δ 29.9, 31.0, 34.7, 35.9, 105.1, 118.8, 128.1, 129.0, 142.5, 142.8, 149.0; IR (KBr) 2220 (CN), 1260 cm^{-1}; UV–vis (pentane) 284 nm (ε 10 300), 416 (5400); MS m/z 488 (M^+, 16%), 261 (21), 260 (100), 228 (94); HRMS 488.2954, calcd for $C_{30}H_{40}N_4S$ 488.2972. Anal. Calcd for $C_{30}H_{40}N_4S$: C, 73.73; H, 8.25; N, 11.46; S, 6.56. Found: C, 73.62; H, 8.50; N, 11.33; S, 6.76. **6**: mp 80.0–80.5 °C; ^1H NMR (90 MHz) δ 1.26 (s, 9 H), 1.42 (s, 9 H), 4.51 (bs, 2 H), 7.36 (AB q, 2 H, Δδ = 0.18 ppm, J = 2.20 Hz); ^{13}C NMR (125 MHz) δ 29.4, 31.2, 34.1, 34.6, 97.5, 118.8, 126.5, 128.8, 133.6. 140.5, 145.5; IR (KBr) 3500, 3450 (NH_2), 2220 (CN), 1635, 1480 cm^{-1}; UV–vis (pentane) 246 nm (ε 6300), 319 (4000); MS m/z 230 (M^+, 22%), 216 (17), 215 (100); HRMS 230.1773, calcd for $C_{15}H_{22}N$ 230.1781. Anal. Calcd for $C_{15}H_{22}N$: C, 78.21; H, 9.53; N, 12.16. Found: C, 78.02; H, 9.56, N, 12.12. **7**: mp 197.0–198.0 °C; ^1H NMR (90 MHz) δ 1.36 (s, 9 H), 1.44 (s, 18 H), 1.65 (s, 9 H), 7.53 (AB q, 2 H, Δδ = 0.19 ppm, J = 1.95 Hz); ^{13}C NMR (22.5 MHz) δ 30.3, 30.9, 31.1, 31.1, 34.9, 35.5, 36.1, 36.3, 105.5, 114.1, 116.2, 124.5, 127.9, 129.2, 130.5, 142.5, 143.1, 143.5, 149.1, 156.4, 162.3; IR (KBr) 2240 (CN), 1240 cm^{-1}; UV–vis (hexane) 328 nm (ε 7800), 519 (21 900); MS m/z 520 (M^+, 57%), 463 (9), 292 (16), 260 (45), 245 (32), 236 (39), 228 (63), 215 (92), 213 (100). Anal. Calcd for $C_{30}H_{40}N_4S_2$: C, 69.19; H, 7.74; N, 10.76; S, 12.31. Found: C, 68.98; H, 7.63; N, 10.85; S, 12.58.

All the photochemical reactions of **2** in other solvents were carried out in a manner similar to the photolysis of **2** in hexane.

Photolysis of 5 in Ethanol. An ethanol solution (70 mL) of sulfur diimide **5** (84 mg, 0.17 mmol) was irradiated by a medium-pressure mercury lamp (100 W) with a Pyrex filter for 3 h at 0 °C under nitrogen. After removal of the solvent, the residue was chromatographed (flash column chromatography, silica gel, hexane–ether (10:1)). The starting material (79 mg, 94%) was recovered in the first fraction. The second fraction gave aniline **6** (3 mg, 3%).

Photolysis of 2 in Argon and Undecane Matrices. The apparatus and experimental technique used in the present study have been described in detail by McMahon et al.[33] The apparatus consisted of three components: a refrigeration unit (a Daikin Industries V2026L and an Air Products IR 02-A cryogenic refrigeration system), a vacuum system, and a gas handling system, all mounted on a movable cart. A cesium iodide plate was attached to the high-conductivity cupper holder inside the cryostat for IR measurement and a sapphire plate for UV–vis measurement. The cryostat was equipped with optical windows, quartz for irradiation and for UV–vis measurement and potassium bromide for IR measurement. The temperature of mounting plate was measured by a 0.07% iron doped gold vs chromel thermocouple. Temperature regulation of the plate was achieved by a small resistive heater surrounding the cold tip. The heater was connected to a Scientific Instruments Series 5500 IEEE-488 STATUS temperature controller.

Azidoisothiazole **2** was introduced from the direct insertion tube warmed to 40 °C for the vaporization. The matrix material was introduced from the gas-handling system. **2** and matrix material were deposited onto the window simultaneously. The irradiation for photochemical reactions was performed by using an Ushio UI-501C (500 W) connected with an Ushio HB-50106AA-A stabilizer. A HOYA UV-32 filter was used for the cut of shorter wavelength irradiation (<320 nm),

(31) Carlsen, L. *J. Org. Chem.* **1976**, *41*, 2971.
(32) Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902.
(33) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

and a drum of 6-cm water layer was used for the cut of thermal irradiation. IR spectra were recorded with a Hitachi 270-30 spectrophotometer, and UV–vis spectra were recorded with a Jasco UVDEC-610 spectrophotometer.

IR Study on the Photolysis of 2 in Argon Matrix. The deposition of argon and **2** was carried out for 2 h to the cesium iodide window at 12 K. IR spectra were observed soon after the irradiation was stopped at 12 K. When the matrix was irradiated for 5 min at 12 K, the absorption of starting azide **2** (2130 cm^{-1}) disappeared and the absorption due to a cyano group (2225 cm^{-1}) appeared. The warming of the sample to 40 K after the irradiation brought no change in the IR spectrum. The observation of the IR spectra was impossible above 40 K because of the decomposition of argon matrices (Figure 2).

IR Study on the Photolysis of 2 in Undecane Matrix. An undecane matrix of **2** was formed by deposition of undecane and azide **2** for 1 h in a manner similar to that in argon matrix. The matrix was irradiated for 10 min at 12 K. Although a small amount of starting azide remained, the absorption due to a cyano group (2225 cm^{-1}) appeared. The matrix was warmed gradually to 110 K after the irradiation. The absorptions at 1200 and 1120 cm^{-1} disappeared at 70 K. The matrix began to decompose when it was warmed to 196 K, and spectroscopic observation was impossible above 196 K (Figure 3).

UV–vis Study on the Photolysis of 2 in Argon Matrix. For the UV–vis monitoring of the photoreaction of **2**, the deposition of argon and **2** on the sapphire window was achieved in a manner similar to the IR experiment for 10 min. UV–vis spectra were observed soon after the irradiation was stopped at 12 K. When the matrix was irradiated for 2 min at 12 K, the absorption of the starting azide (354 nm) disappeared and the absorption of an intermediate (456 and 483 nm) appeared. The absorption coefficient of the intermediate was estimated assuming that the absorption coefficient of the starting azide (354 nm) in argon matrix is equal to that in a pentane solution. The spectrum remained unchanged up to 40 K during the warming of the matrix after the irradiation. The observation of the electronic spectrum was impossible above 40 K because of decomposition of the matrix (Figure 1).

UV–vis Study on the Photoreaction of 2 in Organic Glasses. An Oxford CF204 continuous-flow cryostat system was used for this study. The irradiation for the photoreaction was performed by the same lamp as that used in the IR experiments. UV–vis spectra were recorded with a Jasco UVDEC-610 spectrophotometer.

(a) In EPA Matrix. An EPA solution of azidoisothiazole **2** (concentration 2.19×10^{-4} M) degassed by freeze–thaw cycles was cooled to 70 K in the cryostat. The EPA matrix of **2** was irradiated for 20 min, resulting in the disappearance of the starting azide and the formation of an intermediate (λ_{max} 460 and 484 nm, ϵ 3700 and 3700, respectively). When the sample was warmed to 100 K after the irradiation, the spectrum was changed to that without any absorption band in wavelengths longer than 400 nm. The spectrum remained unchanged up to 120 K, but it changed to the spectrum of sulfur diimide **5** during the warming from 120 to 170 K. Then the sample was warmed to room temperature. The yield of **5** was estimated to be 64% from the absorption coefficient (Figure 4).

(b) In Various Glass Matrices. UV–vis experiments in 3-methylpentane and isopentane (1:9) were carried out in a manner similar to that in EPA matrix. Absorption bands of an intermediate (λ_{max} 458 and 488 nm, ϵ 3300 and 3800, respectively) appeared after 20-min irradiation of **2** at 70 K in 3-methylpentane matrix. When the sample was warmed to 100 K after irradiation, the spectrum underwent a remarkable change to give a new one (λ_{max} 365 nm, ϵ 4600). When **2** was irradiated at 72 K in isopentane (isopentane–3-methylpentane (9:1)) matrix, the spectrum with an absorption band around 470 nm was not observed but a spectrum with absorption bands at 299, 312, and 360 nm was observed.

Preparation of *N,N'*-Bis(2,4-di-*tert*-butyl-6-cyanophenyl)diaminosulfur (11). To an ethereal solution (30 mL) of sulfur diimide **5** (177 mg, 0.36 mmol) was added a solution (50 mL of ether and 5 mL of ethanol) of sodium borohydride (55 mg, 1.45 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature, and then additional ethanol (5 mL), methanol (4 mL), and sodium borohydride (20 mg, 0.53 mmol) were added to the reaction mixture. After being refluxed for 15 min, the reaction mixture was poured into water and extracted with ether. The organic layer was dried, evaporated, and chromatographed (dry column chromatography, silica gel, hexane–ether (5:1)). The first fraction afforded *N,N'*-bis(2,4-di-*tert*-butyl-6-cyanophenyl)diaminosulfur (**11**) (124 mg, 69%). The second fraction gave aniline **6** (36 mg, 21%). **11** was recrystallized from hexane to give colorless crystals. **11**: mp 196.0–197.0 °C; ^{1}H NMR (500 MHz) δ 1.31 (s, 18 H), 1.47 (s, 18 H), 7.17 (bs, 2 H), 7.53 (s, 4 H); ^{13}C NMR (125 MHz) δ 30.4, 31.1, 34.4, 34.8, 102.8, 121.3, 128.5, 129.5, 139.3, 144.3, 147.2; IR (KBr) 3400 (NH), 2200 (CN), 1435, 1225 cm^{-1}; UV–vis (EPA) 226 nm (ϵ 76 000), 261 (22 000), 319 (9300); MS *m/z* 490 (M^+, 9%), 260 (32), 230 (26), 215 (100); HRMS 230.1773, calcd for $C_{15}H_{22}N$ 230.1781. Anal. Calcd for $C_{30}H_{42}N_4S$: C, 73.42; H, 8.63; N, 11.42; S, 6.53. Found: C, 73.51; H, 8.66; N, 11.50; S, 6.40.

Thermolysis of 2 in Hexane. A hexane solution (35 mL) of azidoisothiazole **2** (53 mg, 0.18 mmol) was heated for 1 h at 60 °C. The reaction mixture was evaporated and chromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)). The first fraction gave unsymmetrical sulfur diimide **7** (6 mg, 11%). The second fraction gave symmetrical sulfur diimide **5** (33 mg, 72%). The third fraction afforded aniline **6** (6 mg, 14%). When the thermal reaction of **2** was carried out for 3 days at room temperature (hexane, 60 mL; **2**, 52 mg, 0.18 mmol), **5** (22 mg, 50%), **6** (17 mg, 40%), and **7** (3 mg, 7%) were obtained.

Thermolysis of 2 in Ethanol. An ethanol solution (40 mL) of **2** (57 mg, 0.20 mmol) was heated for 1 h at 60 °C. The reaction mixture was evaporated and chromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)). The first fraction gave **7** (5 mg, 10%). The second fraction gave **5** (9 mg, 18%). The third fraction afforded **6** (31 mg, 68%).

Thermal Reaction of 2 with 2,3-Dimethyl-1,3-butadiene. A hexane solution (75 mL) of **2** (76 mg, 0.26 mmol) and the butadiene (2.18 g, 26.5 mmol) was stirred for 3 days at room temperture. After removal of the solvent, the residue was chromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)). The first fraction gave **7** (3 mg, 4%). The second fraction afforded white crystals of 2-(2',4'-di-*tert*-butyl-6'-cyanophenyl)-4,5-dimethyl-3,6-dihydro-2*H*-1,2-thiazine (**12**) (13 mg, 14%). The third and fourth fractions gave **5** (7 mg, 10%) and **6** (45 mg, 75%), respectively. **12**: mp 152.0–153.2 °C; ^{1}H NMR (500 MHz) δ 1.30 (s, 9 H), 1.41 (s, 9 H), 1.66 (s, 3 H), 1.84 (s, 3 H), 2.96 (d, 1 H, J = 16 Hz), 3.25 (d, 1 H, J = 16 Hz), 3.83 (d, 1 H, J = 16 Hz), 4.26 (d, 1 H, J = 16 Hz), 7.56 (AB q, 2 H, $\Delta\delta$ = 0.17 ppm, J = 2.50 Hz); ^{13}C NMR (125 MHz) δ 17.2, 19.5, 30.1, 31.1, 34.9, 36.1, 37.0, 57.1, 104.1, 114.0, 124.0, 126.6, 129.6, 130.1, 149.0, 149.7, 150.1; IR (KBr) 2230 (CN), 1640 (C=C) cm^{-1}; MS *m/z* 342 (M^+, 48%), 260 (100), 245 (29), 228 (42); HRMS 342.2119, calcd for $C_{21}H_{30}N_2S$ 342.2127.

Thermal Reaction of 2 with Diphenyldiazomethane (14a). A hexane solution (100 mL) of **2** (50 mg, 0.17 mmol) and **14a** (173 mg, 0.89 mmol) was stirred for 3 days at room temperature. After removal of the solvent, the residue was chromatographed (liquid chromatography) to afford 2,4-di-*tert*-butyl-6-cyano-*N*-(α-phenylbenzylidene)aniline (**15a**) (53 mg, 78%). **15a** was recrystallized from ethanol to give yellow crystals. **15a**: mp 98.5–99.0 °C; ^{1}H NMR (500 MHz) δ 1.25 (s, 9 H), 1.47 (s, 9 H), 7.36 (AB q, 2 H, $\Delta\delta$ = 0.45 ppm, J = 1.95 Hz), 7.37 (m, 10 H); ^{13}C NMR (125 MHz) δ 29.9, 31.1, 34.5, 36.3, 101.2, 119.0, 127.1, 127.8, 130.3, 141.4, 146.0, 150.1, 168.0; IR (KBr) 2220 (CN), 1620, 1440 cm^{-1}; UV–vis (hexane) 254 nm (ϵ 14 000), 318 (sh, 3000), 370 (sh, 1400); MS *m/z* 394 (M^+, 35%), 379 (16), 337 (4), 317 (100); HRMS 394.2392, calcd for $C_{28}H_{30}N_2$ 394.2407. Anal. Calcd for $C_{28}H_{30}N_2$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.19; H, 7.71; N, 7.10.

Thermal Reaction of 2 with Diazofluorene (14b). A hexane solution (100 mL) of **2** (50 mg, 0.17 mmol) and **14b** (166 mg, 0.86 mmol) was stirred for 3 days at room temperature. After removal of the solvent, the residue was chromatographed (liquid chromatography) to afford 2,4-di-*tert*-butyl-6-cyano-*N*-fluorenylideneaniline (**15b**) (54 mg, 80%). **15b** was recrystallized from ethanol to give yellow crystals. **15b**: mp 209.0–209.5 °C; ^{1}H NMR (500 MHz) δ 1.23 (s, 9 H), 1.29 (s, 9 H), 7.45 (m, 8 H), 7.52 (AB q, 2 H, $\Delta\delta$ = 0.22 ppm, J = 2.19 Hz); ^{13}C NMR (125 MHz) δ 29.4, 31.3, 34.7, 35.9, 101.5, 118.1, 127.6, 128.6, 132.4, 139.6, 146.9, 150.8, 164.7; IR (KBr) 2230 (CN), 1655, 1600, 1460 cm^{-1}; UV–vis (hexane) 293 nm (ϵ 11 100), 303 (13 500), 396 (1500); MS *m/z* 392 (M^+, 81%), 377 (100), 199 (18), 180 (48), 165 (24), 152 (16), 57 (19); HRMS 392.2266, calcd for $C_{28}H_{28}N_2$ 392.2253.

Thermal Reaction of 2 with 2,2,6,6-Tetramethyldiazocyclohexane (14c). A hexane solution (100 mL) of **2** (50 mg, 0.17 mmol) and **14c**[34] (136 mg, 0.82 mmol) was stirred for 3 days at room temperature. After removal of the solvent, the residue was chromatographed (flash column chromatography, silica gel, pentane–ether) to afford a reddish orange viscous oil of 2,2,6,6-tetramethyl-1-[*N*-(2',4'-di-*tert*-butyl-6'-cyanophenyl)sulfinimidoyl]cyclohexane (**17c**) (68 mg, 98%). **17c**: ^{1}H NMR (500 MHz) δ 1.29 (s, 9 H), 1.39 (s, 9 H), 1.40 (s, 6 H), 1.57–1.66 (m, 4 H), 1.63 (s, 6 H), 1.68–1.74 (m, 2 H), 7.43 (AB q, 2 H, $\Delta\delta$ = 0.14 ppm, J = 2.33 Hz); ^{13}C NMR (125 MHz) δ 17.8, 26.3, 29.6, 31.1, 33.1, 34.4, 36.0, 39.2, 40.3, 41.2, 41.7, 103.6, 120.5, 127.9, 128.0, 143.6, 144.1, 152.3, 183.9; IR (KBr) 2220 (CN), 1420, 1230, 960 (C=S=N) cm^{-1}; UV (hexane) 323 nm (ϵ 6600), 405 (2300); MS *m/z* 398 (M^+, 47%), 262

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(21), 260 (100), 245 (18), 230 (20), 215 (28), 213 (42), 171 (14), 169 (24); HRMS 398.2755, calcd for $C_{25}H_{38}N_2S$ 398.2753.

Thermal Reaction of 2 with 2,2,5,5-Tetramethyldiazocyclopentane (14d). A hexane solution (250 mL) of **2** (250 mg, 0.87 mmol) and **14d**[34] (410 mg, 2.7 mmol) was stirred for 2 days at 30 °C. After removal of the solvent, the residue was chromatographed (liquid chromatography) to afford 2,2,5,5-tetramethyl-1-[*N*-(2′,4′-di-*tert*-butyl-6′-cyanophenyl)-sulfinimidoyl]cyclopentane (**17d**) (180 mg, 54%), which was recrystallized from ethanol to give red crystals. Other fractions were rechromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)) to afford **5** (20 mg, 10%), **6** (40 mg, 20%), and **7** (4 mg, 2%). **17d**: mp 90.0–90.2 °C; ^{1}H NMR (400 MHz) δ 1.28 (s, 9 H), 1.35 (s, 6 H), 1.38 (s, 9 H), 1.61 (s, 6 H), 1.75–1.85 (m, 4 H), 7.42 (AB q, 2 H, $\Delta\delta$ = 0.15 ppm, J = 2.20 Hz); ^{13}C NMR (100 MHz) δ 24.9, 29.8, 30.7, 31.2, 34.6, 36.0, 39.9, 40.4, 48.8, 51.2, 104.9, 120.5, 128.0, 144.3, 144.4, 185.6; IR (KBr) 2200 (CN), 1420, 1230, 960 (C=S=N) cm^{-1}; UV (hexane) 257 nm (ϵ 3800), 275 (2100), 328 (9100), 400 (6100); MS m/z 384 (M$^+$, 19%), 354 (21), 260 (69), 245 (33), 230 (25), 215 (100), 213 (45), 171 (31), 156 (23), 109 (66), 57 (73). Anal. Calcd for $C_{24}H_{34}N_2S$: C, 74.95; H, 9.43; N, 7.28; S, 8.34. Found: C, 74.85; H, 9.32; N, 7.49; S, 8.80.

Thermal Reaction of 2 with 2-Diazo-1,1,3,3-tetramethylindan (14e). A hexane solution (200 mL) of azidoisothiazole **2** (200 mg, 0.69 mmol) and **14e**[34] (280 mg, 1.4 mmol) was stirred for 2 days at 30 °C. After removal of the solvent, the residue was chromatographed (liquid chromatography) to afford 2-(2′,4′-di-*tert*-butyl-6′-cyanophenyl)-5-(1″,1″,3″,3″-tetramethyl-2-indenylidene)-1,2,3,4-thiatriazoline (**16e**) (100 mg, 34%), which was recrystallized from ethanol to give orange crystals. Other fractions were rechromatographed (preparative thin-layer chromatography, silica gel, hexane–ether (5:1)) to afford **5** (20 mg, 11%), **6** (50 mg, 31%), and **7** (4 mg, 2%). **16e**: mp 117.0–117.5 °C; ^{1}H NMR (400 MHz) δ 1.30 (s, 9 H), 1.42 (s, 9 H), 1.65 (s, 6 H), 1.90 (s, 6 H), 7.18–7.24 (m, 2 H), 7.30–7.32 (m, 2 H), 7.46 (AB q, 2 H, $\Delta\delta$ = 0.15 ppm, J = 2.57 Hz); ^{13}C NMR (100 MHz) δ 25.9, 29.8, 31.2, 34.0, 34.5, 36.1, 51.0, 54.4, 105.0, 120.2, 121.9, 122.3, 127.7, 128.0, 128.0, 128.1, 144.4, 144.9, 147.0, 148.2, 152.6, 183.5; IR (KBr) 2220 (CN), 1430, 1235, 960 cm^{-1}; UV (hexane) 256 nm (ϵ 6400), 270 (6700), 328 (10200), 395 (4900); MS m/z 432 (M$^+$, 8%), 400 (1), 354 (5), 260 (69), 215 (63), 213 (45), 172 (67), 157 (100), 57 (59); HRMS 432.2591, calcd for $C_{28}H_{36}N_2S$ 432.2598. Anal. Calcd for $C_{28}H_{36}N_4S$: C, 73.00; H, 7.88; N, 12.16; S, 6.96. Found: C, 72.86; H, 7.83; N, 11.76; S, 6.87.

Thermal Reaction of 2 with Molecular Oxygen in Hexane. A hexane solution (60 mL) of **2** (30 mg, 0.11 mmol) was heated for 5 h at 40 °C with oxygen being bubbled. After removal of the solvent, the residue was chromatographed (liquid chromatography). The first and second fractions gave **7** (3.8 mg, 14%) and **5** (3.6 mg, 14%), respectively. The third fraction afforded a yellow viscous oil of 2,4-di-*tert*-butyl-6-cyano-7,8,9-oxathiazabicyclo[4.3.0]nona-2,4,9-triene 8-oxide (**19**) (8.8 mg, 30%), which was recrystallized from ethanol to give pale yellow crystals. The fourth fraction afforded 2,4-di-*tert*-butyl-6-cyano-*N*-sulfinylaniline (**18**) (3.1 mg, 11%), which was recrystallized from hexane (−78 °C) to give yellow crystals. Finally the fifth fraction gave **6** (3.5 mg, 15%). **18**: mp 97.5–98.0 °C; ^{1}H NMR (500 MHz) δ 1.13 (s, 9 H), 1.39 (s, 9 H), 7.64 (AB q, 2 H, $\Delta\delta$ = 0.14 ppm, J = 1.95 Hz); ^{13}C NMR (125 MHz) δ 29.5, 31.1, 35.0, 35.8, 107.2, 117.9, 127.6, 128.9, 129.0, 139.5, 142.1, 150.6; IR (KBr) 2210 (CN), 1590, 1180 cm^{-1}; UV (hexane) 285 nm (sh, ϵ 15000), 300 (sh, 2600), 375 (2000); MS m/z 276 (M$^+$, 12%), 261 (38), 228 (14), 213 (40), 157 (33), 57 (100); HRMS 276.1299, calcd for $C_{15}H_{20}N_2OS$ 276.1297. Anal. Calcd for $C_{15}H_{20}N_2OS$: C, 65.18; H, 7.29; N, 10.14; S, 11.60. Found: C, 65.15; H, 7.29; N, 10.26; S, 11.54. **19**: mp 114.0–115.0 °C; ^{1}H NMR (500 MHz) δ 1.33 (s, 9 H), 1.43 (s, 9 H), 5.99 (d, 1 H, J = 1.85 Hz), 6.62 (d, 1 H, J = 1.85 Hz); ^{13}C NMR (125 MHz) δ 28.9, 29.0, 35.1, 35.6, 87.6, 113.7, 117.9, 133.8, 143.1, 149.1, 176.5; IR (KBr) 1600, 1490, 1190 (S=O) cm^{-1}; UV (hexane) 310 nm (ϵ 1900), 345 (1500); MS m/z 292 (M$^+$, 13%), 218 (44), 215 (15), 213 (15), 188 (13), 182 (16), 57 (100); HRMS 292.1241, calcd for $C_{15}H_{20}N_2O_2S$ 292.1244. Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.62; H, 6.89; N, 9.58; S, 10.97. Found: C, 61.63; H, 6.84; N, 9.84; S, 10.91.

Photochemical Reaction of 2 with Molecular Oxygen. A hexane solution (70 mL) of **2** (82 mg, 0.29 mmol) was irradiated by a medium-pressure mercury lamp with a Pyrex filter for 30 min at 0 °C. After removal of the solvent, the residue was chromatographed (liquid chromatography) to afford **7** (2 mg, 2%), **5** (24 mg, 34%), **18** (16 mg, 20%), and **6** (11 mg, 17%).

Thermal Reaction of 2 with Molecular Oxygen in Ethanol. An ethanol solution (70 mL) of **2** (70 mg, 0.24 mmol) was heated for 3 h at 40 °C with oxygen being bubbled. After removal of the solvent, the residue was chromatographed (liquid chromatography) to give a colorless viscous oil of ethyl *N*-(2,4-di-*tert*-butyl-6-cyanophenyl)sulfamate (**25**) (28 mg, 34%), **19** (2 mg, 2%), and **6** (30 mg, 54%). **25**: ^{1}H NMR (400 MHz) δ 1.35 (s, 9 H), 1.48 (t, 3 H, J = 7.2 Hz), 1.50 (s, 9 H), 4.50 (q, 2 H, $\Delta\delta$ = 0.035 ppm, J = 7.2 Hz), 6.51 (bs, 1 H), 7.46 (AB q, 2 H, $\Delta\delta$ = 0.18 ppm, J = 2.40 Hz); ^{13}C NMR (100 MHz) δ 14.6, 31.0, 31.8, 35.0, 36.4, 68.6, 114.4, 117.8, 129.6, 130.5, 132.8, 148.7, 151.6; IR (KBr) 3250 (NH), 2240 (CN), 1360, 1180 (SO_2) cm^{-1}; UV (ethanol) 308 nm (ϵ 2500); MS m/z 338 (M$^+$, 25%), 323 (12), 230 (44), 215 (100), 57 (29); HRMS 338.1663, calcd for $C_{17}H_{26}N_2O_3S$ 338.1664.

Photolysis of 19. A solution (hexane (25 mL) and ether (10 mL) of **19** (25 mg) was irradiated by a medium-pressure mercury lamp with a Pyrex filter for 1 h at 0 °C. Removal of the solvent afforded a complex mixture, from which no identifiable product was obtained.

Thermal Reaction of 19 in Ethanol. An ethanol solution of **19** (24 mg) was heated for 3 h at 40 °C. Removal of the solvent resulted in the recovery of the starting compound **19** (20 mg, 80%).

Thermal Reaction of 2 with Phenylthiirane (26). A hexane solution (67 mL) of **2** (100 mg, 0.35 mmol) and **26** (410 mg, 2.7 mmol) was stirred for 2 days at 30 °C. After removal of the solvent, the residue was chromatographed at 0 °C (flash column chromatography, silica gel, pentane–ether). The first fraction afforded a reddish purple solid of *N*-2,4-di-*tert*-butyl-6-cyano-*N*-thiosulfinylaniline (**27**) (32 mg, 31%). **27** was recrystallized from hexane (−78 °C) to give deep reddish purple crystals, which were thermally unstable at room temperature. The other fractions were **7** (4 mg, 5%), **5** (11 mg, 13%), and **6** (17 mg, 22%). **27**: mp 75.0–76.0 °C dec; ^{1}H NMR (400 MHz) δ 1.36 (s, 9 H), 1.37 (s, 9 H), 7.70 (AB q, 2 H, $\Delta\delta$ = 0.17 ppm, J = 2.2 Hz); ^{13}C NMR (100 MHz) δ 29.5, 31.1, 35.1, 35.8, 102.5, 117.9, 127.8, 129.4, 140.9, 148.0, 150.5; IR (KBr) 2230 (CN), 1600, 1240, 1000, 880, 700, 650 cm^{-1}; UV (isopentane) 286 nm (ϵ 5400), 341 (6300), 449 (2700); MS m/z 292 (M$^+$, 4%), 277 (2), 260 (4), 245 (7), 236 (100), 221 (26), 215 (31), 213 (55); HRMS 292.1036, calcd for $C_{15}H_{20}N_2S_2$ 292.1067.

Registry No. 1, 127204-55-1; **2**, 127204-57-3; **3**, 63335-28-4; **4**, 138235-22-0; **5**, 122204-58-4; **6**, 17582-88-6; **7**, 127616-57-3; **10**, 138235-23-1; **11**, 138235-24-2; **12**, 138235-25-3; **14a**, 883-40-9; **14b**, 832-80-4; **14c**, 89050-90-8; **14d**, 71690-98-7; **14e**, 81331-45-5; **15a**, 127616-58-4; **15b**, 127616-63-1; **16e**, 138235-26-4; **17c**, 127616-59-5; **17d**, 138235-27-5; **18**, 127616-60-8; **19**, 127616-61-9; **25**, 138259-03-7; **26**, 1498-99-3; **27**, 127616-62-0; 2,3-dimethyl-1,3-butadiene, 513-81-5.