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Physical Properties and Various Reactions of Thionitrites and Related Substances

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Several new sulfenyl or sulfonyl derivativives, thionitrates ($RSNO_2$), sulfonyl nitrites (RSO_2NO), were successfully isolated by treating corresponding thiols and sulfinic acids with dinitrogen tetraoxide (N_2O_4). Spectroscopic data of both stable and many rather unstable compounds were determined and compared with those of corresponding alkyl nitrites (RONO) or alkyl nitrates ($RONO_2$). Chemical reactivities of these uncommon, novel *S*-nitroso and *S*-nitro compounds were investigated.

Preparation of Thionitrites and Related Substances. We reported recently that various thionitrites (RSNO) (**2**) were prepared quantitatively by the reaction of thiols (**1**) with dinitrogen tetraoxide (N_2O_4)[1,2] (Eq. 1). Red colored thionitrites **2** were not so stable as to be isolated in pure form except *t*-alkyl or *s*-alkyl derivatives.

We found that stable *t*-alkyl thionitrates (**3a**—**c**) can be prepared in good yields by treating thiols with excess dinitrogen tetraoxide (Eq. 2). *t*-Pentyl thionitrate (**3b**) and 1,1-dimethylheptyl thionitrate (**3c**) are new additions in the literature. We also found that the novel aryl thionitrates (**3d**—**f**) can be isolated as unstable white crystals upon treating the corresponding thiols with excess dinitrogen tetraoxide in hexane at low temperatures (*ca.* −60 °C). However, these aryl thionitrates **3d**—**f** were found to decompose readily at room temperature. All the *t*-alkyl thionitrates **3a**—**c** were stable at room temperature and some aryl thionitrates **3d**—**e** were stable at low temperature, however, other thionitrates were found to be not stable enough to be isolated in pure form. Reaction

$$\underset{\mathbf{1}}{RSH} \xrightarrow{1\ eq.\ N_2O_4} \underset{\mathbf{2}}{RSNO} \qquad (1)$$

$$\underset{\mathbf{1}}{RSH} \xrightarrow{excess\ N_2O_4} [RSNO] \longrightarrow \underset{\mathbf{3}}{RSNO_2} \qquad (2)$$

$$\underset{\mathbf{4}}{RSO_2H} \xrightarrow{1-2\ eq.\ N_2O_4} \underset{\mathbf{5}}{RS(\uparrow O)(\downarrow O)\text{-}NO} + \underset{\mathbf{6}}{RSO_3H} \qquad (3)$$

1a, **2a**, **3a**: R=*t*-Bu
1b, **3b**: R=*t*-C_5H_{11}
1c, **3c**: R=1,1-dimethylheptyl
4a, **5a**, **6a**: R=CH_3
1d, **3d**, **4b**, **5b**, **6b**: R=*p*-Tolyl
4c, **5c**, **6c**: R=Ph
1e, **3e**, **4d**, **5d**, **6d**: R=*p*-Cl-C_6H_4
1f, **3f**, **4e**, **5e**, **6e**: R=*p*-Br-C_6H_4
4f, **5f**, **6f**: R=*p*-CH_3O-C_6H_4

conditions and isolated yields of thionitrates **3a**—**f** are listed in Table 1.

Sulfonyl nitrites (**5**) were considered to be the reaction intermediates in the reaction of sulfinic acids with alkyl nitrites.[3] Nevertheless these compounds have not been isolated. We now have found that sulfonyl nitrites **5a**—**f**, new sulfonyl derivatives, can be isolated as brown unstable crystals upon treating sulfinic acids (**4a**—**f**) with dinitrogen tetraoxide. Corresponding sulfonic acids (**6a**—**f**) were also obtained nearly in the same yields (Eq. 3). Sulfonyl nitrites **5a**—**f** isolated had strong SO_2 absorption bands near 1840 cm^{-1}. Mass spectrum of sulfonyl nitrite **5b** showed the corresponding fragment ion peaks: *m/e* (rel intensity), 155 (9, *p*-Tol†SO_2^+), 91 (20, *p*-Tol^+), and 30 (100, NO^+). However, no molecular ion peak was observed due to the weak S–N bond of this compound.

Spectroscopic Data of Thionitrites and Related Substances. Spectroscopic data of *t*-butyl nitrite (**7**), *t*-butyl nitrate (**8**), *t*-butyl thionitrite (**2a**), *t*-butyl thionitrate (**3a**) and methanesulfonyl nitrite (**5a**) were obtained and compared with each other. Infrared absorption bands of these compounds are listed in Table 3. Thionitrite **2a** and thionitrate **3a** showed the infrared absorption bands at longer wavelengths than corresponding alkyl nitrite **7** and alkyl nitriate **8**. The same trend is known in C=O stretching of ester and thioester, and is explained in terms of the electronegativity difference between S and O.[4] This inductive effect may also play a major role in our case.[5] Thus the presence of a strongly electronegative sulfonyl group may be responsible for the shift of N=O stretching frequency of sulfonyl nitrite **5a** up to 1842 cm^{-1}. In this case lack of resonance between S and N may be partly responsible for the large wave number because

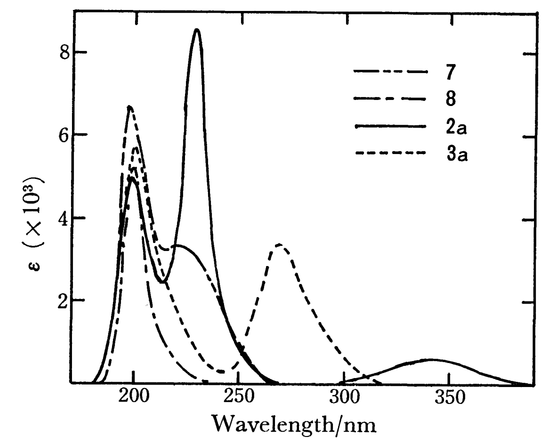


Fig. 1. UV spectra of *O*- and *S*-nitroso or nitro compounds.

† Tol=tolyl.

TABLE 1. REACTIONS OF THIOLS **1a**—**f** WITH EXCESS DINITROGEN TETRAOXIDE

Thiol	Solvent	$[N_2O_4]^{a)}/[RSH]$	Reaction temp/°C	Reaction time/min	Product	Isolated yield/%
1a	Ether	2.5	25	30	**3a**	84
1b	Ether	2.5	25	20	**3b**	55
1c	Ether	2.5	25	15	**3c**	48
1d	Hexane	1.5	−60	5	**3d**	86
1e	Hexane	1.5	−60	5	**3e**	65
1f	Hexane	1.5	−60	5	**3f**	73

a) Mole ratio.

TABLE 2. REACTIONS OF SULFINIC ACIDS **4a**—**f** WITH DINITROGEN TETRAOXIDE

Sulfinic acid	$[N_2O_4]^{a)}/[RSO_2H]$	Reaction temp/°C	Reaction time/min	Product	Isolated yield/%
4a	1.5	0	3[b)]	**5a**	55
4b	2	0	10	**5b**	54
4c	2	−20	120	**5c**	38
4d	2	0	10	**5d**	47
4e	2	0	7	**5e**	38
4f	4	0	10	**5f**	44

a) Mole ratio. b) After stirring for 3 min at 0 °C sulfonyl nitrite **5a** precipitated out at −60 °C.

TABLE 3. IR ABSORPTION BANDS OF *O*- AND *S*-NITROSO OR NITRO COMPOUNDS

Compound	Absorption bands (cm^{-1})			
	NO	*asym* NO_2	*sym* NO_2	O-N or probably S-N
7	1620			800, 755
8		1608	1292	860
2a	1490			760
3a		1510	1300, 1257	820
5a	1842			a)

a) Several absorption bands were observed at 750—960 cm^{-1}.

the sulfur atom in sulfonyl nitrite **5a** has no lone pair to conjugate with nitroso group.

^{1}H-NMR of alkyl nitrite **7**, alkyl nitrate **8**, thionitrite **2a** and thionitrate **3a** were measured. Chemical shifts are listed in Table 4. Chemical shifts of *t*-butyl groups of thionitrite **2a** and thionitrate **3a** shifted toward the lower fields than corresponding alkyl nitrite **7** and alkyl nitrate **8** due to the effect of sulfur atom. UV spectra of these compounds were also recorded and shown in Fig. 1, while the numerical values of the UV spectra are listed in Table 5. Thionitrite **2a** showed a rather strong absorption at a visible wavelength region and had a greenish red color. Alkyl nitrite **7** showed a very weak absorption at a visible wavelength. All these compounds had N=O or NO_2 absorption bands at 250—180 nm.

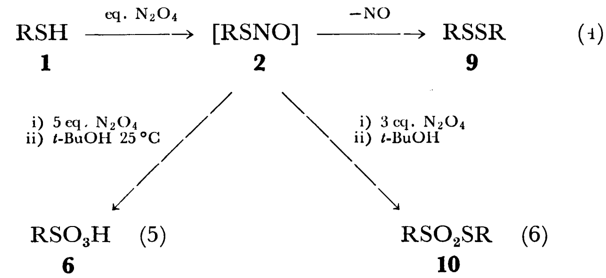
Chemical Reactivities and Synthetic Applications of Thionitrites. Both aromatic and alkyl thiols (**1d**, **1j**, **1k**, **1l**, **1e**, **1g**, **1h**, and **1i**) reacted readily with excess

TABLE 4. ^{1}H-NMR CHEMICAL SHIFTS OF *t*-BUTYL GROUPS IN *O*- AND *S*-NITROSO OR NITRO COMPOUNDS

Compound	Chemical shift of *t*-butyl group (CCl_4, ppm)
7	1.60
8	1.54
2a	1.85
3a	1.58

TABLE 5. UV SPECTROSCOPIC DATA OF *O*- AND *S*-NITROSO OR NITRO COMPOUNDS

Compound	Wavelength/nm (ε)
7	196 (6700), 219 (3300), 339 (28), 351 (48), 397 (57)
8	201 (5200), 380 (87), 397 (57)
2a	198 (5000), 228 (8600), 342 (630)
3a	201 (5700), 268 (3400)



1a: R=*t*-Bu
1d, **6a**, **9b**, **10b**: R=*p*-Tolyl
1j, **2c**, **6b**, **9a**, **10c**: R=Ph
1k, **10d**: R=*m*-Tolyl
1l, **10e**: R=*o*-Tolyl
1e, **10f**: R=*p*-Cl-C_6H_4
1g, **10g**: R=*p*-NO_2-C_6H_4
1h, **10h**: R=cyclohexyl
1i, **10i**: R=*n*-C_8H_{17}

dinitrogen tetroxide at a low temperature to afford the corresponding thiosulfonic *S*-esters (**10b**—**i**) in good yields (Eq. 6). Symmetrical thiosulfonic *S*-esters have generally been synthesized by the oxidation of disulfides[6)] or by the reaction of sulfinic acids with sulfenyl chlorides.[7)] These methods, however, involve two or more reaction steps and form such side products as thiosulfonic *S*-esters and sulfonic acids. Our new method is simple and involves only one pot reaction. When thiols **1d**, **1j**, **1k**, **1l**, **1e**, **1g**, **1h**, and **1i** were mixed with excess dinitrogen tetraoxide at *ca.* −20—0 °C and then quenched with *t*-butyl alcohol, the corresponding thiosulfonic *S*-esters **10b**—**i** were obtained

Table 6. Reactions of thiols with dinitrogen tetraoxide

Thiol	Reaction time/min	Reaction temp/°C	$\frac{[N_2O_4]^{a)}}{[RSH]}$	Product	Isolated yield/%
1a	5	25	4	**3a**	87
1d	5	−20	4	**10b**	65
1j	5	−20	4	**10c**	88
1k	1	0	4	**10d**	65
1l	1	0	4	**10e**	77
1e	5	−20	4	**10f**	77
1g	1	0	4	**10g**	70
1h	5	−20	4	**10h**	62
1i	1	0	4	**10i**	60
1j	3	−70	1	**9a**	*ca.* 100
1j	120	25	6	**6a**	*ca.* 100
1d	120	25	6	**6b**	*ca.* 100

a) Mole ratio.

in good yields in such an inert solvent as ethyl ether. A solution of dinitrogen tetraoxide (in CCl_4) was added to a solution of a certain thiol in anhydrous ethyl ether at *ca.* −20 °C. Immediately, the mixture colored to bright red, characteristic of thionitrite **2**, which solution was stirred further for 1—5 min until the red color disappeared. The mixture was quenched with *t*-butyl alcohol. The *crude* product was purified by a preparative TLC. The results are summarized in Table 6. The yields of the thiosulfonic *S*-ester **10b—i** were markedly high when the reaction temperature was controlled at *ca.* −20 °C and quenched with excess *t*-butyl alcohol.

When the reaction mixture of thiol **1j** with dinitrogen tetraoxide was quenched with methanol or isopropyl alcohol instead of *t*-butyl alcohol, methyl benzenesulfinate (**13a**) (22% of yield) or isopropyl benzenesulfinate (**13b**) (10% of yield) was obtained at the expense of the intermediate such as benzenesulfinyl nitrite (**12**), which is probably in an equilibrium with phenyl thionitrate (**3g**), and methanol or isopropyl alcohol probably attacks the sulfinyl sulfur atom to form the corresponding sulfinate (Eq. 7). However,

$$\underset{\mathbf{1j}}{\text{PhSH}} \xrightarrow[-20\,^\circ\text{C in ether}]{\text{eq. }N_2O_4} \underset{\mathbf{2c}}{[\text{PhS-N=O}]} \xrightarrow[-20\,^\circ\text{C}]{N_2O_4}$$

$$\underset{\mathbf{3g}}{[\text{PhSNO}_2]} \rightleftarrows \underset{\mathbf{11}}{[\text{PhSONO}]} \rightleftharpoons \underset{\mathbf{12}}{[\text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{-NO}]} \xrightarrow{\text{R'OH}}$$

$$\underset{\mathbf{13}}{\text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{OR}'} + \text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{SPh}\ \mathbf{10} + \underset{\mathbf{9a}}{\text{PhSSPh}} \qquad (7)$$

13a: R′=Me
13b: R′=Me_2CH

bulky *t*-butyl alcohol may not attack the sulfinyl sulfur atom due to the steric hindrance. When the reaction mixture was quenched with *t*-butyl alcohol, *t*-butyl benzenesulfinate could not be detected. Probably, homolytic scission of the unstable intermediate **12** may form the sulfinyl radical which is converted to the corresponding diphenyl α-disulfoxide (**14**), which then would be converted to the corresponding *S*-phenyl benzenethiosulfonate (**10c**)[8,9] (Eq. 8).

$$\mathbf{12} \rightarrow \text{NO} + \text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\cdot \rightarrow \underset{\mathbf{14}}{[\text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{-}\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{Ph}]} \rightarrow \text{Ph}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{SPh} \qquad (8)$$

Meanwhile treatment of the thiol **1d**, and **1j** with 6 eq. dinitrogen tetraoxide at room temperature followed by quenching with excess *t*-BuOH gave the sulfonic acids (**6a,b**) quantitatively (Eq. 5), whereas treatment of thiol **1j** with 1 eq. with dinitrogen tetraoxide at −70 °C gave diphenyl disulfide (**9a**) quantitatively after decomposition of unstable phenyl thionitrite(**2c**) at room temperature (Eq. 4). Treatment of thiol **1a** with 3 eq. dinitrogen tetraoxide, however, gave thionitrate **3a** in an excellent yield. Therefore, the corresponding thiosulfonic *S*-ester **10b—i**, sulfonic acids **6a,b**, and disulfide **9a** can be prepared selectively by the simple and selective oxidation of the thiol **1** with dinitrogen tetraoxide when the reaction temperature, time and the concentration of dinitrogen tetraoxide are carefully controlled.

We reported in the previous paper that thionitrites reacted with thiols to afford the unsymmetrical disulfides nearly quantitatively.[2] When thionitrites **2a,b** were allowed to react with sodium benzenethiolate (**15**), the corresponding unsymmetrical disulfides (**16a, b**) were also obtained in good yields (Eq. 9).

$$\underset{\mathbf{2}}{\text{RSNO}} + \underset{\mathbf{15}}{\text{PhSNa}} \longrightarrow \underset{\mathbf{16}}{\text{RSSPh}} \qquad (9)$$

2a, **16a**: R=*t*-Bu **2b**, **16b**: R=*p*-Tolyl

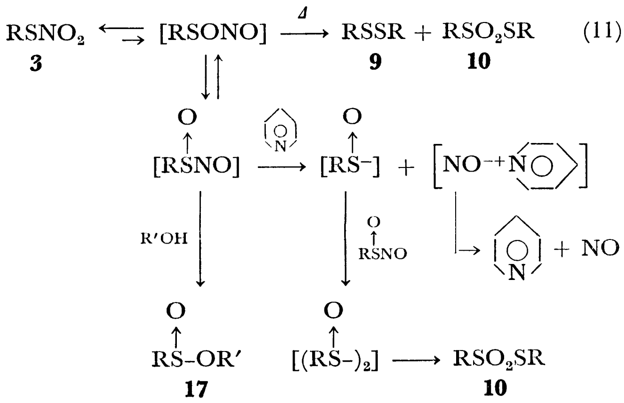
Chemical Reactivities and Synthetic Applications of Thionitrates. Thionitrate **3a**, one of the stable thionitrates, was also found to react with benzenthiolate **15** at room temperature to afford *t*-butyl phenyl disulfide (**16c**) in 69% isolated yield (Eq. 10).

$$\underset{\mathbf{3a}}{t\text{-BuSNO}_2} + \underset{\mathbf{15}}{\text{PhSNa}} \xrightarrow[\text{in MeOH, 40 min}]{} \underset{\mathbf{16c}}{t\text{-BuSSPh}} \qquad (10)$$

When thionitrate **3a** was heated in carbon tetrachloride for 1 h at 130 °C in a sealed tube, di-*t*-butyl disulfide (**9c**) was obtained as the major product, whereas decomposition of thionitrate **3d** at room temperature gave thiosulfonic *S*-ester **10b** as the main product together with a small amount of disulfide **9b** (Eq. 11). On the other hand, when thionitrates **3a**, **3d**, and **3e** were treated with a catalytic amount of pyridine, corresponding thiosulfonic *S*-esters **10j**, **10b**, and **10k** were obtained selectively in good yields (Eq. 12). Evolution of NO gas was confirmed by GC mass-spectroscopic analysis. When thionitrate **3d** was quenched with excess methanol, methyl *p*-toluenesulfinate **17** was obtained in 17% yiled (Eq. 13).

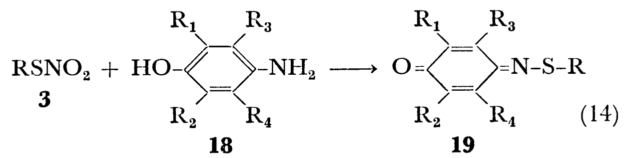
We also found that the reaction of isolated thionitrates **3a—e** with various *p*-aminophenols (**18a—i**) readily afforded the corresponding *N*-(*t*-alkylthio)-*p*-benzoquinone imines (**19a—i**) (Eqs. 14 and 15).

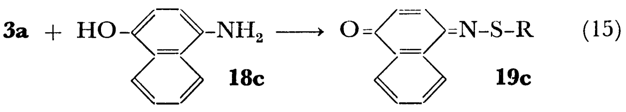
Only a few *N*-(alkylthio)-*p*-benzoquinone imines were prepared previously from *N*-chloro-*p*-benzoquinone imines and thiols.[10] Our new synthetic method of quinone imines **19a**—**i** is simple and especially useful for the syntheses of *N*-*t*-alkylthio derivatives.



(13) (12)

3a, **9c**, **10j**: R=*t*-Bu **3e**, **10k**: R=*t*-C_5H_{11}
3d, **9b**, **10b**: R=*p*-Tolyl **17**: R=*p*-Tolyl, R′=CH_3





18a, **19a**: R=*t*-Bu, $R_1=R_2=R_3=R_4=H$
18b, **19b**: R=*t*-Bu, $R_3=CH_3$, $R_1=R_2=R_4=H$
18d, **19d**: R=*t*-Bu, $R_1=R_2=CH_3$, $R_3=R_4=H$
18e, **19e**: R=*t*-Bu, $R_1=R_2=Cl$, $R_3=R_4=H$
18f, **19f**: R=*t*-C_5H_{11}, $R_1=R_2=R_3=R_4=H$
18g, **19g**: R=1,1-dimethylheptyl, $R_1=R_2=R_3=R_4=H$
18h, **19h**: R=*p*-Cl-C_9H_4, $R_1=R_2=R_3=R_4=H$
18i, **19i**: R=*p*-Br-C_6H_4, $R_1=R_2=R_3=R_4=H$

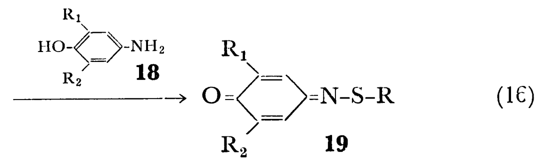
TABLE 7. REACTIONS OF THIONITRATES WITH AMINOPHENOLS

Aminophenol	Thionitrate	Product	Isolated yield/%
18a	**3a**	**19a**	40
18b	**3a**	**19b**	45, 46[a)]
18c	**3a**	**19c**	15, 16[b)]
18d	**3a**	**19d**	47
18e	**3a**	**19e**	45
18f	**3b**	**19f**	40
18g	**3c**	**19g**	33
18h	**3e**	**19h**	18[d)]
18i	**3f**	**19i**	11[d)]
18j	**3h**	**19j**	10[c,d)]
18k	**3d**	**19k**	6[c,d)]

a) In this case $CuCl_2$ was not added. Chromatographic separation gave a poor result and the yield was determined by GLC. b) HCl salt was used as the starting material. c) An oxidative mixture of the thiol with 2 eq. N_2O_4 was used due to the instabilities of these thionitrates. d) $CuCl_2$ was not used in these cases for instabilities of these thionitrates in the presence of $CuCl_2$.

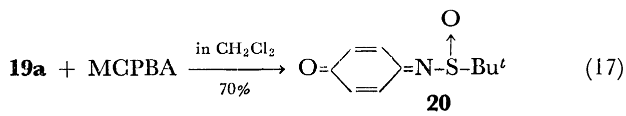
An oxidative mixture of *s*-BuSH (**1m**) or thiol **1d** with excess dinitrogen tetraoxide probably contains *s*-butyl thionitrate (**3h**) or thionitrate (**3d**), respectively, because of the formation of *N*-(*s*-butylthio)-*p*-benzoquinone imine (**19j**) or *N*-(*p*-tolylthio)-*p*-benzoquinone imine (**19k**) from the corresponding *p*-aminophenols (**18j**, **18k**) (Eq. 16). All these new compounds **19a**—**k** are quite stable and have vivid yellow colors due to the strong absorption band ($\varepsilon_{max}>10^4$) near 400 nm. Structures of the products **19a**—**k** were identified by IR, NMR, UV, and mass spectrocopies. Elemental analyses of these compounds **19a**—**k** all agree with these formulae. Isolated yields of compounds **19a**—**k** are listed in Table 7.

$$\underset{\mathbf{1}}{RSH} + \text{excess } N_2O_4 \longrightarrow \underset{\mathbf{3}}{[RSNO_2]}$$



1m, **3h**: R=*s*-Bu
1d, **3d**: R=*p*-Tolyl
18j, **19j**: R=*s*-Bu, $R_1=R_2=Cl$
18k, **19k**: R=*p*-Tolyl, $R_1=R_2=H$

When compound **19a** was oxidized with an equivalent amount of *m*-chloroperbenzoic acid, a red colored unstable *N*-(*t*-butylsulfinyl)-*p*-benzoquinone imine **20** was obtained (70%) upon column chromatography (Eq. 17). This sulfinyl derivative **20** showed a strong absorption at 1080 cm^{-1} (SO) in IR spectrum, however, was found to decompose readily (*ca.* 1 h) at room temperature.



We also found that thionitrate **3a** reacted readily with octylamine (**21**) at room temperature for 10 min to give *N*-(*t*-butylthio)octylamine (**22**) in a good yield (Eq. 18).

$$\underset{\mathbf{3a}}{t\text{-BuSNO}_2} + \underset{\mathbf{21}}{n\text{-}C_8H_{17}NH_2} \rightarrow \underset{\mathbf{22}}{n\text{-}C_8H_{17}NHS\text{-}Bu^t} \quad (18)$$

Chemical Reactivities of Sulfonyl Nitrites. When *p*-toluenesulfonyl nitrite (**5b**) was heated in dioxane or neat, vigorous evolution of gas was observed and white crystals were obtained. After recrystallization from acetic acid, elemental analysis of this crystalline compound showed the formula of $(p\text{-TolSO}_2)_3(NO)$ (**23**)[11)] and IR spectroscopic data and melting point were identical with those of a known compound which was reported as tris(*p*-tolylsulfonyl)amine oxide by Kresze and Kort.[3)] Other several sulfonyl nitrites **5a**, **5c**, **5d**, and **5e** were also found to undergo thermodecomposition to give white crystals described as formula $(RSO_2)_3(NO)$ (**23a**, **23c**—**e**) by elemental analyses (Eq. 19). However, since the compound **23a** gives two distinctly different peaks of metyl groups on both ^1H and ^{13}C-NMR spectra (integral ratio=2:1 on^1 H-NMR), the structure of these compounds **23a**—**e**

Table 8. Thermal decomposition of sulfonyl nitrites **5a**—**e**

Sulfonyl nitrite	Reaction time/min	Reaction temp/°C	Solvent	Product	Isolated yield/%
5a	5	70—80	None	**23a**	44
5b	10	90—100	None	**23b**	59
5b	3	60—80	Dioxane	**23b**	64
5c	15	60—90	None	**23c**	52
5d	10	90—100	None	**23d**	62
5e	10	90—100	None	**23e**	65

$$\underset{\mathbf{5}}{3\,RSO_2NO} \longrightarrow \underset{\mathbf{23}}{(RSO_2)_3(NO)} + 2\,NO \qquad (19)$$

5a, 23a: $R=CH_3$ **5d, 23d**: $R=p\text{-}Cl\text{-}C_6H_4$
5b, 23b: $R=p$-Tolyl **5e, 23e**: $R=p\text{-}Br\text{-}C_6H_4$
5c, 23c: R = Ph

is belived to be represented by $(RSO_2)_2N\text{-}O\text{-}SO_2R$ rather than $(RSO_2)_3NO$, and further detailed structure assignment is now underway. Meanwhile, the gas formed by thermal decomposition of sulfonyl nitrite **5b** showed a strong peak at *m/e* 30 (NO) in its mass spectrum. These results are listed in Table 8.

Sulfonyl nitrites **5a**—**e** were unstable compounds in protic solvents such as alcohols or thiols and decomposed in a few minutes (Eqs. 20 and 21). When sulfonyl nitrite **5b** was stirred in methanol, *N*,*N*-bis(*p*-tolylsulfonyl)hydroxylamine (**24**) was obtained in a good yield. Sulfonyl nitrite **5b** also reacted with thiol **1a** in dioxane to give hydroxylamine **24**. The reaction

$$\underset{\mathbf{5b}}{2\,p\text{-}TolSO_2NO} + MeOH \rightarrow \underset{\mathbf{24}}{(p\text{-}TolSO_2)_2NOH} + MeONO \qquad (20)$$

$$\underset{\mathbf{5b}}{2\,p\text{-}TolSO_2NO} + \underset{\mathbf{1a}}{t\text{-}BuSH} \rightarrow \mathbf{24} + \underset{\mathbf{2a}}{t\text{-}BuSNO} \qquad (21)$$

mixture of sulfonyl nitrite **5b** and thiol **1a** was found to turn to red in a few minutes due undoubtedly to the formation of thionitrite **2a**.

Sulfonyl nitrite **5b** also reacted with thionitrite **2a** in dioxane to give *S*-*t*-butyl *p*-toluenethiosulfonate (**25**) in 20% yield (Eq. 22). This reaction was slow and

$$\underset{\mathbf{5b}}{p\text{-}TolSO_2NO} + \underset{\mathbf{2a}}{t\text{-}BuSNO} \xrightarrow[1-3\,h]{25\,°C} \underset{\mathbf{25}}{p\text{-}Tol\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}S\text{-}Bu^t} \qquad (22)$$

required for over 1 h at room temperature.

When sulfonyl nitrite **5b** was reduced with sodium borohydride, *N*-(*p*-tolylsulfonyl)hydroxylamine (**26**) was obtained in 16% yield (Eq. 23). Other major product was compound **23b**.

$$\mathbf{5b} + \text{excess } NaBH_4 \rightarrow \underset{\mathbf{26}}{p\text{-}Tol\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}NHOH} + \mathbf{23b} \qquad (23)$$

Experimental

All the melting points and boiling points were uncorrected. Elemental analysis of sulfur was carried out by Sagami Chemical Research Center and the analyses of other elements were carried out by the Chemical Analysis Center at this University. Analytical determination by GLC were performed on a Hitachi 163 gas chromatograph fitted with the following column (3 mm o.d. × 3 m): 10% SE-30 on Chromosorb W. ^{1}H-NMR spectra were taken at 60 MHz on a Hitachi R-24A apparatus. ^{13}C-NMR spectra were measured on a Bruker FXD 4-100 NMR spectrometer. Mass spectra were recorded with a Hitachi RMU-6M spectrometer.

The following compounds were obtained according to the known procedures which are described in the literature: Dinitrogen tetraoxide,[2)] **8**,[12)] **4a**,[13)] **4d**,[14)] **4e**,[15)] **4f**.[16)]

t-Butyl Thionitrite (2a). Dinitrogen tetraoxide[2)] (0.1 mol) in carbon tetrachloride (11 ml) was added to a stirred solution of thiol **1a** (9.02 g, 0.1 mol) in dry ethyl ether (100 ml) for a few minutes at −70 °C. The solution was stirred further for several minutes and poured into the cold 5% $NaHCO_3$ aq solution and extracted with ethyl ether. The ethereal extract was dried ($MgSO_4$) in dark at 0 °C, and the solvent was evaporated *in vacuo* giving almost pure thionitrite **2a** (7.0 g, 59%), which was pure enough for the reaction over several months at −20 °C with molecular sieves: (lit,[17)] bp 36 °C/48 mmHg). IR (neat): 1490 (NO), 1360, 1298, 1157, and 760 cm^{-1}. NMR (CCl_4): δ=1.85 (s). Thionitrite **2a** was usually used without distillation.

Other thionitrites were prepared similarly by the method already reported by Oae *et al.*[2)] Generally thionitrites were not stable enough to be isolated in pure form, and they were usually used in ethereal solution after washing (5% aq $NaHCO_3$ solution) and drying ($MgSO_4$).

t-Butyl Thionitrate (3a). The following is a typical procedure to prepare stable *t*-alkyl thionitrates.

This reaction required a relatively large flask (2 l) fitted with a reflux condenser, which is open for air escape, since the reaction took place vigorously. Dinitrogen tetraoxide[2)] (1.5 mol) in carbon tetrachloride (135 ml) was added dropwise to a stirred solution of thiol **1a** (55.3 g, 0.6 mol) in dry ethyl ether (500 ml) for over 30 min at the rate that ethyl ether slowly refluxed. After the addition was over, the solution was stirred further for *ca.* 30 min. The solution was washed with ice cold water and dried ($MgSO_4$), concentrated, and distilled (with molecular sieves) giving 67.5 g (84%) of thionitrate **3a** which had a stimulant odor.

Spectroscopic data, boiling points and elemental analytical data of stable thionitrates (**3a**—**c**) are listed in Tables 9 and 10.

p-Chlorophenyl Thionitrate (3e). The following is a typical procedure to prepare unstable aryl thionitrates.

Dinitrogen tetraoxide (0.15 mol) in carbon tetrachloride (13.5 ml) was added dropwise to a stirred suspension of thiol **1e** (15.7 g, 0.1 mol) in hexane (100 ml) for 5 min at −60 °C. Immediately the mixture colored to bright red, characteristic of the thionitrite. After the red color of thionitrite disappeared (*ca.* 2—3 min), the white crystalline thionitrate **3e** was collected by filtration in a cold room (*ca.* 0 °C) and recrystallized with ethyl ether at −70 °C to give 13.1 g (65%) of thionitrate **3e**. IR spectrum was measured in a cold room (maintained at *ca.* −20 °C) because of the instability of thionitrate **3e**. IR spectroscopic data and melting points of thionitrate **3d**—**f** were listed in Table 9.

Syntheses of Sulfonyl Nitrites (5a—f). A typical procedure is as follows. A solution of dinitrogen tetraoxide (0.1 mol) in carbon tetrachloride (11 ml) was added to a stirred suspension of sulfinic acid **4b** (15.6 g, 0.1 mol) and dry ethyl ether (50 ml) at 0 °C in a few minutes. The suspension soon turned to a pale brown color in a few minutes forming

TABLE 9. SPECTROSCOPIC DATA AND MELTING POINTS OF THIONITRATES

Thionitrate	IR (neat, cm^{-1})	NMR (CCl_4, ppm)
3a	1510, 1300, 1263, 1155, 820	1.58 (s)
3b	1510, 1300, 1255, 1150, 821	1.00 (t, 3H, -$CH_2C\underline{H}_3$), 1.33 (s, 6H, -$C\underline{H}_3$), 1.70 (q, 2H, -$C\underline{H}_2$-)
3c	1510, 1297, 1250, 1130, 813	0.73—2.33 (m, 11H), 1.45 (t, 2H, $C\underline{H}_2CS$), 1.55 (s, 6H, $C\underline{H}_3$)
3d	1510, 1378, 1290, 800	Mp 32—33 °C (dec)
3e	1510, 1378, 1300, 1070, 1000, 810	Mp 44—45 °C (dec)
3f	1510, 1375, 1290, 1055, 1000, 812	Mp 49—50 °C (dec)

TABLE 10. ELEMENTAL ANALYSES AND BOILING POINTS OF STABLE THIONITRATES

Thionitrate	Found (%) C	H	N	Calcd (%) C	H	N	Bp (°C/mmHg)
3a	—			—			40—41/6 (lit,[17] 55/13)
3b	40.05	7.29	9.01	40.24	7.43	9.38	36—38/3
3c	52.94	9.35	6.78	52.65	9.32	6.82	78—81/2

TABLE 11. SPECTROSCOPIC DATA OF SULFONYL NITRITES **5a—f**

Sulfonyl nitrile	IR (KBr, cm^{-1}) NO	SO_2	NMR ($CDCl_3$, ppm) CH_3	Ring proton
5a	1842	1355, 1157	3.36 (br, s)	
5b	1850	1390, 1185	2.37 (s, 3H)	7.10 (d, J=8 Hz, 2H), 7.50 (d, J=8 Hz, 2H)
5c	1860, 1840	1390, 1190		7.21—7.85 (m, 4H)
5d	1859, 1835	1398, 1195		7.39 (d, J=10 Hz, 2H), 7.68 (d, J=10 Hz, 2H)
5e	1858, 1835	1390, 1191		7.65 (br, m)
5f	1880, 1860	1382, 1195	3.90 (s, 3H)	6.80—7.15 (m, 2H), 7.65—8.05 (m, 2H)

the precipitate of sulfonyl nitrite **5b**. The mixture was stirred further for 10 min at 0 °C. Then the brown precipitate was filtered, washed with dry ethyl ether and dried *in vacuo* giving 11.2 g (61%) of pure sulfonyl nitrite **5b**. IR and NMR spectra of sulfonyl nitrites **5a—f** are listed in Table 11, while elemental analyses of sulfonyl nitrites **5b—e** are listed in Table 12.

*Thiosulfonic S-Ester (**10b—i**).* A typical procedure is as follows. A solution of dinitrogen tetraoxide (20 mmol, in CCl_4) was added to a solution of thiol **1e** (723 mg, 5.0 mmol) in anhydrous ethyl ether (15 ml) with stirring at *ca.* 0 °C in the dark. Immediately, the mixture colored to

TABLE 12. ELEMENTAL ANALYSES OF SULFONYL NITRITES **5b—e**[a)]

Compound	Found (%)[b)] C	H	N	S	Calcd (%) C	H	N	S
5b	45.43	3.76	7.37	17.16	45.39	3.80	7.56	17.31
5c	42.40	2.89	7.68	18.59	42.10	2.94	8.18	18.73
5d	35.43	1.97	6.36	15.73	35.04	1.96	6.81	15.59
5e	29.10	1.57	5.22	—	28.81	1.61	5.61	—

a) Compounds **5a** and **5f** were too unstable to be analyzed. b) Nitrogen contents of compounds **5b—e** were found to be in smaller values (0.19—0.50%) due to the gradual generation of NO gas at room temperature.

TABLE 13. SPECTROSCOPIC DATA AND MELTING POINTS OF THIOSULFONIC *S*-ESTER **10b—i**

Compound	(IR cm^{-1}) *asym* SO_2	*sym* SO_2	NMR (CCl_4, ppm)	Mp/°C
10b	1320	1137	2.33 (s, 6H), 6.9—7.5 (m, 8H)	76—78 (lit,[19] 78.5—79.5)
10c	1325	1143	7.0—7.7 (m)	44—45 (lit,[18] 45)
10d	1325	1138	2.26 (s, 3H), 2.27 (s, 3H), 6.9—7.5 (m, 8H)	Oil (lit,[20] Oil)
10e	1321	1143	2.16 (s, 3H), 2.63 (s, 3H), 6.9—7.5 (m, 8H)	52—54 (lit,[18] 55—56)
10f	1323	1139	7.2—7.5 (m)	135—136 (lit,[21] 138)
10g	1343	1142	7.3—8.5	176—178 (lit,[22] 180—180.5)
10h	1332	1135	0.7—2.5 (m, 20H), 2.9 (br, m, 1H), 3.3 (br, m, 1H)	Oil (lit,[23] 37—38)
10i	1325	1129	0.7—2.1 (m, 30H), 2.9—3.3 (m, 4H)	Oil (lit,[24] Oil)

bright red, characteristic of the thionitrite, which was stirred further for 1 min until the red color disappeared. The mixture was quenched with *t*-butyl alcohol (5 ml) for several minutes at 0—20 °C and then washed with 5% aq $NaHCO_3$ solution to remove nitric acid formed during the reaction. The *crude* product from the organic layer was purified by preparative TLC (silica gel, hexane:ether=20:1) to give 615 mg (77%) of thiosulfonic *S*-ester **10f**.

Spectroscopic data of thiosulfonic *S*-esters **10b—i** are summarized in Table 13. Melting points or boiling points of thiosulfonic *S*-esters **10b—i** were identical with those of literatures.

*p-Toluenesulfonic Acid (**6a**).* A solution of dinitrogen tetraoxide (15 mmol, in CCl_4) was added to a solution of thiol **1d** (310 mg, 2.5 mmol) in anhydrous ethyl ether (7.5 ml) with stirring at *ca.* 0 °C. The solution was further stirred for 2.5 h at room temperature. After quenching the solution with *t*-butyl alcohol (5 ml) for 5 min, the volatile material was evaporated *in vacuo* giving 487 mg (quantitative) of sulfonic acid **6a**. IR and NMR spectra were identical with those of authentic samples.

*Diphenyl Disulfide (**9a**).* Dinitrogen tetraoxide (5 mmol, in CCl_4) was added to a stirred solution of thiol **1j** (550 mg, 5 mmol) in dry ethyl ether (10 ml) at −70 °C. After a few minutes the red colored solution was poured into the 5% $NaHCO_3$ aq solution. After the mixture was warmed to room temperature. After the red color of the thionitrite disappeared, the ethereal layer was separated, dried ($MgSO_4$) and evaporated giving 540 mg (quantitative) of disulfide **9a**. Spectroscopic data were identical with those of authentic sample.

Methyl Benzenesulfinate (13a) and Isopropyl Benzenesulfinate (13b). Dinitrogen tetraoxide (7.6 mmol, in CCl_4) was added to a solution of thiol **1j** (421 mg, 3.8 mmol) at −20 °C. After a few minutes, the solution was quenched with methanol (1.2 ml) and stirred further for 5 min at 0 °C. After evaporation of the solvent and TLC (hexane:ether=10:1) gave 65 mg (22%) of sulfinate **13a**: bp (bath temp) 90—100 °C/2 mmHg (lit,[25] 76—81 °C/0.45 mmHg). IR (neat): 1130 (SO), 965, 758, and 696 cm^{-1}. NMR (CCl_4): δ=3.33 (s, 3H, $-CH_3$) and 7.54 (m, 5H, ring-protons). Other isolated products were disulfide **9a** (25%) and *S*-phenyl thiosulfonate (**10**) (43%), and spectroscopic data of these compounds were identical with those of authentic samples.

Sulfinate **13b** was also isolated by a similar procedure: bp (bath temp) 120—130 °C/2 mmHg (lit,[26] 110—117 °C/0.5 mmHg). IR (neat): 1143 (SO), 1102, 920, 845, and 735 cm^{-1}. NMR (CCl_4): δ=1.13 (d, J=6 Hz, 3H, $-CH_3$), 1.34 (d, J=6 Hz, 3H, $-CH_3$), 4.14 (m, 1H, CH), and 7.47 (m, 5H, ring-protons). Other isolated products were disulfide **9a** (20%) and thiosulfonic *S*-ester **10c** (42%).

Disulfides (16a—c). Dinitrogen tetraoxide (5 mmol, in CCl_4) was added to a stirred solution of thiol **1d** (620 mg, 5 mmol) in 10 ml of ethyl ether at −70 °C. After a few minutes, 5% aq $NaHCO_3$ solution was added and extracted with 10 ml of ethyl ether. The ethereal solution was dried ($MgSO_4$) and filtered at 0 °C. Sodium benzenethiolate **15** (661 mg, 5 mmol) in methanol (6 ml) was added to the ethereal solution and the solution was stirred for 12 h at −10 °C. The solution was washed with $NaHCO_3$ aq solution and dried ($MgSO_4$). The solvent was evaporated and water was added. The mixture was extracted with ethyl ether. Ethereal extract was dried and evaporated to give 898 mg (77%) of disulfide **16a**.

A similar treatment of thionitrite **2a** or thionitrate **3a** with benzenethiolate **15**, gave disulfide **16b** (74%) and **16c** (69%), respectively. Stable thionitrite **2a** and stable thionitrate **3a** were used after purification, unlike unstable thionitrite **2b**.

IR and NMR spectroscopic data of disulfides **16a—c** were identical with those of authentic samples.

Thermal Decomposition of t-Butyl Thionitrate (3a). The solution of thionitrate **3a** (30 mg, 0.22 mmol) in carbon tetrachloride (0.25 ml) was heated in an oil bath at 130 °C in a sealed tube for NMR. After 1 h, NMR spectrum showed that nearly all the starting material was converted to di-*t*-butyl disulfide **9c**: NMR, IR, and mass spectroscopic data were identical with those of authentic sample.

Reactions of Thionitrates (3a, 3c, and 3d) with Pyridine. Thionitrate **3a** 1.89 g (14 mmol) was added dropwise to a stirred solution of pyridine (554 mg, 7 mmol) in carbon tetrachloride (20 ml) for 5 min. The solution was stirred further for 30 min. Distillation gave 1.03 g (70%) of thiosulfonic *S*-ester **10j**, 280 mg of pyridine, and 246 mg of solid which could not be characterized. Thiosulfonic *S*-ester **10j**: mp 22—24 °C, bp (bath temp) 80 °C/5 mmHg. IR (neat): 1445, 1360, 1290 (SO_2), 1140, and 1100 cm^{-1} (SO_2). NMR (CCl_4): δ=1.40 and 1.58. MS (70 eV), *m/e* (rel intensity), 210 (1, M^+), 89 (10, t-BuS^+), and 57 (100, t-Bu^+). Found: C, 45.59; H, 8.61; S, 30.29%. Calcd for $C_8H_{18}O_2S_2$: C, 45.68; H, 8.62; S, 30.48%.

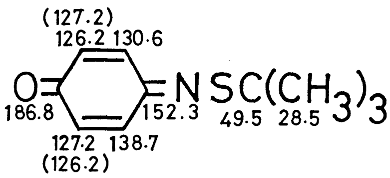
Thiosulfonic *S*-ester **10b** (65%) and thiosulfonic *S*-ester **10k** (89%) were obtained from thionitrate **3d** and thionitrate **3c**, respectively. IR spectroscopic data of thiosulfonic *S*-ester **10b** were identical with those of authentic sample. Thiosulfonic *S*-ester **10k**: bp (bath temp) 80 °C/3 mmHg. IR (neat): 1455, 1295, and 1100 cm^{-1}. NMR (CCl_4): δ=1.00 (t, 6H, CH_2-CH_3), 1.35 (s, 6H, $SC(CH_3)_2$), and 1.88 (q, 4H, CH_2). Found: C, 50.39; H, 9.43%. Calcd for $C_{10}H_{22}O_2S_2$: C, 50.38; H, 9.30%.

Methyl p-Toluenesulfinate (17). Methanol (5 ml) was added dropwise for a few minutes onto the crystals of thionitrate **3e** at −20 °C. After vigorous reaction, the *crude* material was purified by TLC to give 222 mg (17%) of sulfinate **17**: MS (70 eV) *m/e* (rel intensity), 170 (56, M^+), 139 (100, p-$TolSO_2^+$), and 91 (28, p-Tol^+). IR and NMR spectroscopic data were identical with those of literatures.[27] The other products were the corresponding thiosulfonic *S*-ester **10f** (36%) and di-(*p*-chlorophenyl) disulfide (**9d**) (12%).

N-(t-Butylthio)-p-benzoquinone Imine (19a). *p*-Aminophenol 546 mg (5 mmol) was added for 5 min into a stirred suspension of well-dried anhydrous copper(II) chloride (810 mg, 6 mmol) and thionitrate **3a** (1020 mg, 7.5 mmol) in anhydrous acetonitrile (15 ml). The mixture was stirred for 1 h at room temperature, and then hydrochloric acid solution (20%, 100 ml) was added to the suspension and the mixture was extracted with ethyl ether. The ethereal extract was dried ($MgSO_4$) and evaporated. After purifying the extract on silica gel TLC (hexane:ether=10:1) bright yellow crystals of benzoquinone imine **19a** were obtained (390 mg, 40%).

Compound **19a** was obtained nearly in the same yield, even without copper(II) chloride, however, separation of the products was quite difficult. When *p*-hydroxyaniline was treated with thionitrate **3a** without copper(II) chloride, excess thionitrate **3a** was not converted to corresponding disulfide **9c** but to the thiosulfonic *S*-ester **10j** by undesirable oxidation. Since the thiosulfonic *S*-ester formed was quite difficult to be removed completely unlike the disulfide by distillation or TLC from the benzoquinone imine **19a**, copper(II) chloride is a useful reagent especially in separating benzoquinone imine **19a** in pure form.

The ^{13}C-NMR spectrum (in $CDCl_3$, ppm) of compound **19a** is depicted in the following structure.



UV and IR spectra and elemental analytical data of compound **19a** and its derivatives are listed in Table 14. NMR and mass spectroscopic data of compound **19a** and its derivatives are listed in Tables 15 and 16, respectively.

N-(s-Butylthio)-2,6-dichlorobenzoquinone Imine (19j). Dinitrogen tetraoxide (30 mmol) in carbon tetrachloride (3 ml) was added to a stirred solution of *s*-BuSH (1.35 g, 15 mmol) at 0 °C. The solution turned immediately red, characteristic for *s*-butyl thionitrite and soon the red color disappeared, due undoubtedly to the formation of *s*-butyl thionitrite. Aminophenol **18j** (1.78 g, 10 mmol) was then added for a few minutes and the solution was stirred further for 1.5 h. The mixture was filtered[28] and the filtrate was diluted with ethyl ether, washed with aq $NaHCO_3$ solution, dried ($MgSO_4$), evaporated and the usual TLC separation

TABLE 14. SPECTROSCOPIC DATA (UV, IR) AND ELEMENTAL ANALYSES OF QUINONE IMINES **19a—k**

Compound	UV (hexane, λ_{max}, nm)	IR (νC=O, cm^{-1})	Found (%)				Calcd (%)			
			C	H	N	S	C	H	N	S
19a	401 ($\varepsilon=2.7\times10^4$)	1630	61.38	6.60	7.13	16.29	61.51	6.71	7.17	16.42
19b	399 ($\varepsilon=2.1\times10^4$)	1630	63.48	7.29	6.70	15.36	63.12	7.22	6.69	15.32
19c	418 ($\varepsilon=1.9\times10^4$)	1642	68.53	6.16	5.70	12.90	68.54	6.14	5.78	13.07
19d	405 ($\varepsilon=2.4\times10^4$)	1615	64.29	7.43	6.09	—	64.53	7.67	6.27	—
19e	424 ($\varepsilon=3.4\times10^4$)	1648	45.83	4.16	5.32	—	45.46	4.19	5.30	—
19f	402 ($\varepsilon=2.7\times10^4$)	1632	62.93	7.08	6.34	—	63.12	7.22	6.69	—
19g	405 ($\varepsilon=2.7\times10^4$)	1630	67.54	8.73	4.99	—	67.88	8.73	5.27	—
19h	447 ($\varepsilon=2.2\times10^4$)	1620	58.00	3.16	5.39	—	57.71	3.22	5.60	—
19i	448 ($\varepsilon=2.1\times10^4$)	1630	48.60	2.59	4.37	—	48.99	2.74	4.76	—
19j	425 ($\varepsilon=2.2\times10^4$)	1645	45.68	4.20	5.41	—	45.46	4.19	5.30	—
19k	438 ($\varepsilon=1.7\times10^4$)	1625	68.28	4.73	5.83	—	68.09	4.83	6.10	—

TABLE 15. ^{1}H-NMR SPECTROSCOPIC DATA (CCl_4, ppm) OF QUINONE IMINE **19a—k**

Compound	O=⁄—H	O=⁄=\H	Other proton
19a	6.13—6.50 (m, 2H)	6.75—7.35 (m, 2H)	1.45 (s, 9H, *t*-Bu)
19b	6.24 (s, 1H) 6.34 (dd, *J*=10 Hz, *JJ*=2 Hz, 1 Hz)	7.20 (d, *J*=10 Hz, 1H)	1.47 (s, 9H, *t*-Bu) 2.40 (s, 3H, -C$\underline{H}_3$)
19c	6.57 (d, *J*=10.5 Hz, 1H)	7.32 (d, *J*=10.5 Hz, 1H)	1.52 (s, 9H, *t*-Bu) 7.12—7.60 (m, 2H) 7.89—8.20 (m, 2H)
19d		6.76 (br, s, 1H) 7.00 (br, s, 1H)	1.42 (s, 9H, *t*-Bu) 1.97 (s, 6H, -C$\underline{H}_3$)
19e		7.32 (br, s, 1H) 7.54 (br, s, 1H)	1.50 (s, 9H, *t*-Bu)
19f	6.05—6.47 (m, 2H)	6.66—7.34 (m, 2H)	0.94 (t, 3H, $CH_2C\underline{H}_3$) 1.37 (s, 6H, -C(-)-C$\underline{H}_3$) 1.76 (q, 2H, -C$\underline{H}_2$-)
19g	6.1—6.6 (m, 2H)	6.7—7.5 (m, 2H)	0.6—2.1 (m, 11H)
19h	6.4—6.7 (m, 2H)	6.75—7.63 (m, 6H)[a]	
19i	6.4—6.7 (m, 2H)	6.75—7.55 (m, 6H)[a]	
19j		7.28 (d, *J*=3 Hz, 1H) 7.60 (d, *J*=3 Hz, 1H)	1.07 (t, 3H, $CH_2C\underline{H}_3$) 1.48 (d, *J*=7 Hz, 3H, -CHC$\underline{H}_3$) 1.68—2.20 (m, 1H, S-C$\underline{H}$) 3.10—4.10 (m, 2H, C$\underline{H}_2$)
19k	6.25—6.51 (m, 2H)	6.91—7.89 (m, 6H)[a]	2.42 (s, 3H, -C$\underline{H}_3$)

a) Contains ring proton.

TABLE 16. MASS SPECTROSCOPIC DATA OF QUINONE IMINES **19a—k**

Compound	MS (70 eV), *m/e* (rel intensity)
19a	195 (37, M+), 138 (86), 57 (44)
19b	209 (28, M+), 152 (44), 57 (100)
19c	245 (22, M+), 188 (100), 57 (84)
19d	223 (44, M+), 166 (100), 57 (61)
19e	263 (48, M+), 206 (77), 57 (100)
19f	209 (31, M+), 138 (100), 71 (50)
19g	265 (9, M+), 138 (100), 127 (11)
19h	249 (100, M+), 143 (73)
19i	294 (97, M+), 188 (100)
19j	263 (41, M+), 206 (69), 57 (100)
19k	229 (100, M+), 123 (43), 91 (8)

(hexane:ether=7:1) gave 256 mg (10%) of benzoquinone imine **19j**. Spectroscopic data and elemental analytical data are listed in Tables 14, 15, and 16.

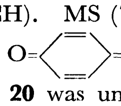
Oxidation of N-(t-*Butylthio*)-p-*benzoquinone Imine* (***19a***) *with* m-*Chloroperbenzoic Acid.* *m*-Chloroperbenzoic acid (360 mg, 1.88 mmol) was added to a stirred solution of benzoquinone imine **19a** in dichloromethane (15 ml) at 0 °C. The solution was further stirred for 30 min at 0 °C. The solvent was evaporated *in vacuo*. Column chromatography (hexane: chloroform=2:1—0:1) gave 276 mg (70%) of sulfinyl derivative **20**. IR (neat): 1080 cm^{-1} (SO). UV (hexane): λ_{max}= 415 nm. NMR (CCl_4): δ=1.32 (s, 9H, *t*-Bu), 6.48 (d, *J*=10 Hz, 2H, O=C-CH), and 6.93 (d, *J*=10 Hz, 2H, O=C-C=CH). MS (70 eV), *m/e* (rel intensity), 211 (1, M+), 154 (100, O==NSO+), and 57 (17, *t*-Bu+). Sulfinyl derivative **20** was unstable at room temperature, and soon

TABLE 17. SPECTROSCOPIC DATA OF COMPOUND **23a—e**

Compound	IR (KBr, cm^{-1}) asym SO_2	IR (KBr, cm^{-1}) sym SO_2	Mp/°C
23a	1380	1175	139—140
23b	1390	1195	190—192
		1175	
23c	1395	1197	99—101
23d	1400	1190	168—170
23e	1395	1192	198—200

TABLE 18. ELEMENTAL ANALYSES OF COMPOUND **23a—e**

Compound	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
23a	13.57	3.23	5.14	13.48	3.39	5.24
23b	51.27	4.05	2.84	50.90	4.27	2.83
23c	47.49	3.24	2.76	47.67	3.33	3.09
23d	39.19	2.20	2.46	38.82	2.17	2.51
23e	31.44	1.60	2.00	31.32	1.75	2.02

decomposed (*ca.* 1 h) to give dark material.

N-(t-Butylthio)octylamine (22). Thionitrate **3a** (2.02 g, 15 mmol) in acetonitrile (10 ml) was added to a stirred solution of amine **21** in acetonitrile (20 ml) for 10 min at 0 °C. The solution was further stirred for 1 h. The solvent was evaporated. TLC (hexane:ether=10:1) gave 524 mg (24%) of sulfenamide **22**: bp (bath temp) 85—95 °C/4 mmHg. IR (neat): 1460, 1135, and 910 cm^{-1}. NMR (CCl_4): δ=0.6—2.0 (m, 15H, $CH_3(CH_2)_6$–), 1.17 (s, 9H, *t*-Bu), 2.36 (br, 1H, NH), and 2.86 (br, 2H, –$C\underline{H}_2$–NH). Found: C, 65.95; H, 12.41; N, 6.32%. Calcd for $C_{12}H_{17}NS$: C, 66.29; H, 12.52; N, 6.44%. The other main product was *t*-$BuSO_2S$-Bu^t (814 mg, 3.87 mmol). Di-*t*-butyl disulfide (180 mg, 1.01 mmol) was also obtained.

Thermal Decomposition of p-Toluenesulfonyl Nitrite (5b). Sulfonyl nitrite **5b** (1.85 g, 10 mmol) in dioxane (25 ml) was stirred for a few minutes at *ca.* 70 °C. Vigorous evolution of gas was observed and the brown color of the solution soon vanished. The solution was concentrated, and the product was recrystallized from acetic acid giving 1.06 g (64%) of compound **23b**. Spectroscopic data, melting points, and elemental analyses of compound **23b** and related compounds are listed in Tables 19 and 20.

N,N-Bis(p-tolylsulfonyl)hydroxylamine (24). *A)*: Sulfonyl nitrite **5b** (185 mg, 10 mmol) was stirred in methanol for 5 min. The solvent was evaporated *in vacuo* to give 170 mg (quantitative) of almost pure hydroxylamine **24**: mp 124—126 °C (from ether), (lit,[3] 126 °C). IR (KBr): 3260 (OH), 1380 (SO_2), 1190 (SO_2), 855, and 673 cm^{-1}. IR spectroscopic data were identical with those of authentic sample prepared by the method in the literature.[3]

B): Sulfonyl nitrite **5b** (185 mg, 10 mmol) was added to a stirred solution of thiol **1a** in dioxane (20 ml). The solution slowly turned red, characteristic for thionitrite **2a**, and the mixture was further stirred for 30 min. Then, volatile materials were evaporated to give 180 mg of hydroxylamine **24**.

S-t-Butyl p-Toluenethiosulfonate (25). Sulfonyl nitrite **5b** (725 mg, 5 mmol) was added to a stirred solution of thionitrite **2a** (595 mg, 5 mmol) in dioxane (20 ml) at 0 °C. The mixture was further stirred for 1 h. Then the mixture was concentrated and upon TLC (hexane:ether=5:1) gave 241 mg of thiosulfonic *S*-ester **25**: mp 68 °C (from ethanol), (lit,[29] 69 °C). IR (KBr): 1591, 1460, 1318, 1140, 811, and 702 cm^{-1}. NMR (CCl_4): δ=1.43 (s, 9H, *t*-Bu), 2.42 (s, 3H, $C\underline{H}_3$), 7.28 (d, *J*=8 Hz, 2H, ring proton), and 7.75 (d, *J*=8 Hz, 2H, ring proton). MS (70 eV), *m/e* (rel intensity), 244 (5, M^+), 187 (9, *p*-$TolSO_2S^+$), 155 (10, *p*-$TolSO_2^+$), 91 (27, *p*-Tol^+), 89 (5, *t*-BuS^+), and 57 (100, *t*-Bu^+).

N-(p-Tolylsulfonyl)hydroxylamine (26). Sodium borohydride 1.89 g (50 mmol) was added to a stirred solution of sulfonyl nitrite **5b** (1.85 g, 10 mmol) in dioxane (25 ml) at 0 °C. The mixture was stirred further for 40 min at *ca.* 5—10 °C, then excess borohydride was decomposed with acetone (10 ml) at 0 °C. After nearly all the volatile material was evaporated *in vacuo* saturated NaCl aq solution was added into the residue, which was extracted with ethyl ether. Etherial extract was dried ($MgSO_4$), evaporated and upon TLC (hexane:ether=2:1) 304 mg (16%) of hydroxylamine **26** was obtained: mp 129—130 °C (recrystallized from benzene and ether). IR (neat): 3360 (OH), 1345 (SO_2), 985, 815, and 730 cm^{-1}. NMR ($CDCl_3$): δ=2.45 (s, 3H, –$C\underline{H}_3$), 3.88 (br, 2H, N$\underline{H}$ and O$\underline{H}$), 7.32 (d, *J*=9 Hz, 2H, ring proton), and 7.82 (d, *J*=9 Hz, 2H, ring proton). Found: C, 44.76; H, 4.73; N, 7.11%. Calcd for $C_7H_9NO_3S$: C, 44.90; H, 4.84; N, 7.48%.

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