

## Physical Properties and Various Reactions of Thionitrites and Related Substances

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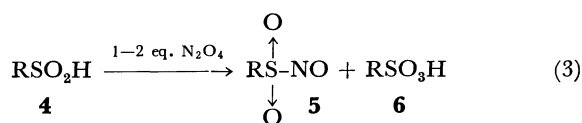
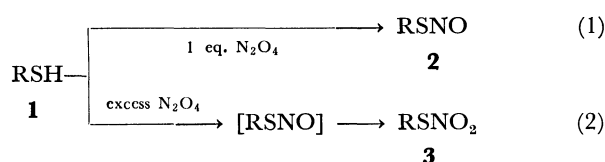
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Several new sulfenyl or sulfonyl derivatives, thionitrates ( $\text{RSNO}_2$ ), sulfonyl nitrites ( $\text{RSO}_2\text{NO}$ ), were successfully isolated by treating corresponding thiols and sulfinic acids with dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ). Spectroscopic data of both stable and many rather unstable compounds were determined and compared with those of corresponding alkyl nitrites ( $\text{RONO}$ ) or alkyl nitrates ( $\text{RONO}_2$ ). 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 ( $\text{RSNO}$ ) (**2**) were prepared quantitatively by the reaction of thiols (**1**) with dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ )<sup>1,2)</sup> (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 tetroxide (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 tetroxide in hexane at low temperatures (*ca.*  $-60^\circ\text{C}$ ). 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



- 1a, 2a, 3a:** R = *t*-Bu  
**1b, 3b:** R = *t*-C<sub>5</sub>H<sub>11</sub>  
**1c, 3c:** R = 1,1-dimethylheptyl  
**4a, 5a, 6a:** R = CH<sub>3</sub>  
**1d, 3d, 4b, 5b, 6b:** R = *p*-Tolyl  
**4c, 5c, 6c:** R = Ph  
**1e, 3e, 4d, 5d, 6d:** R = *p*-Cl-C<sub>6</sub>H<sub>4</sub>  
**1f, 3f, 4e, 5e, 6e:** R = *p*-Br-C<sub>6</sub>H<sub>4</sub>  
**4f, 5f, 6f:** R = *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>

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.<sup>3)</sup> 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 tetroxide. Corresponding sulfonic acids (**6a—f**) were also obtained nearly in the same yields (Eq. 3). Sulfonyl nitrites **5a—f** isolated had strong SO<sub>2</sub> absorption bands near 1840 cm<sup>-1</sup>. Mass spectrum of sulfonyl nitrite **5b** showed the corresponding fragment ion peaks: *m/e* (rel intensity), 155 (9, *p*-Tol<sup>†</sup>SO<sub>2</sub><sup>+</sup>), 91 (20, *p*-Tol<sup>+</sup>), and 30 (100, NO<sup>+</sup>). 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 nitrate **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.<sup>4)</sup> This inductive effect may also play a major role in our case.<sup>5)</sup> 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<sup>-1</sup>. In this case lack of resonance between S and N may be partly responsible for the large wave number because

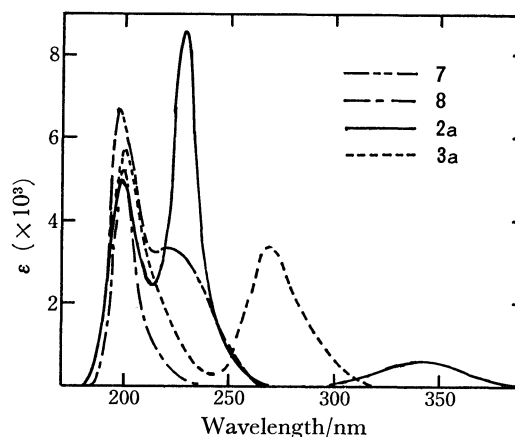


Fig. 1. UV spectra of *O*- and *S*-nitroso or nitro compounds.

† Tol = tolyl.

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

| Thiol     | Solvent | $\frac{[\text{N}_2\text{O}_4]^{\text{a)}}}{[\text{RSH}]}$ | Reaction temp/°C | Reaction time/min | Product   | Isolated yield/% |
|-----------|---------|-----------------------------------------------------------|------------------|-------------------|-----------|------------------|
| <b>1a</b> | Ether   | 2.5                                                       | 25               | 30                | <b>3a</b> | 84               |
| <b>1b</b> | Ether   | 2.5                                                       | 25               | 20                | <b>3b</b> | 55               |
| <b>1c</b> | Ether   | 2.5                                                       | 25               | 15                | <b>3c</b> | 48               |
| <b>1d</b> | Hexane  | 1.5                                                       | −60              | 5                 | <b>3d</b> | 86               |
| <b>1e</b> | Hexane  | 1.5                                                       | −60              | 5                 | <b>3e</b> | 65               |
| <b>1f</b> | Hexane  | 1.5                                                       | −60              | 5                 | <b>3f</b> | 73               |

a) Mole ratio.

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

| Sulfinic acid | $\frac{[\text{N}_2\text{O}_4]^{\text{a)}}}{[\text{RSO}_2\text{H}]}$ | Reaction temp/°C | Reaction time/min | Product   | Isolated yield/% |
|---------------|---------------------------------------------------------------------|------------------|-------------------|-----------|------------------|
| <b>4a</b>     | 1.5                                                                 | 0                | 3 <sup>b)</sup>   | <b>5a</b> | 55               |
| <b>4b</b>     | 2                                                                   | 0                | 10                | <b>5b</b> | 54               |
| <b>4c</b>     | 2                                                                   | −20              | 120               | <b>5c</b> | 38               |
| <b>4d</b>     | 2                                                                   | 0                | 10                | <b>5d</b> | 47               |
| <b>4e</b>     | 2                                                                   | 0                | 7                 | <b>5e</b> | 38               |
| <b>4f</b>     | 4                                                                   | 0                | 10                | <b>5f</b> | 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 <sup>−1</sup> ) |                             |                            |                     |
|-----------|--------------------------------------|-----------------------------|----------------------------|---------------------|
|           | NO                                   | <i>asym</i> NO <sub>2</sub> | <i>sym</i> NO <sub>2</sub> | O–N or probably S–N |
| <b>7</b>  | 1620                                 |                             |                            | 800, 755            |
| <b>8</b>  |                                      | 1608                        | 1292                       | 860                 |
| <b>2a</b> | 1490                                 |                             |                            | 760                 |
| <b>3a</b> |                                      | 1510                        | 1300, 1257                 | 820                 |
| <b>5a</b> | 1842                                 |                             |                            | a)                  |

a) Several absorption bands were observed at 750–960 cm<sup>−1</sup>.

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

<sup>1</sup>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<sub>2</sub> absorption bands at 250–180 nm.

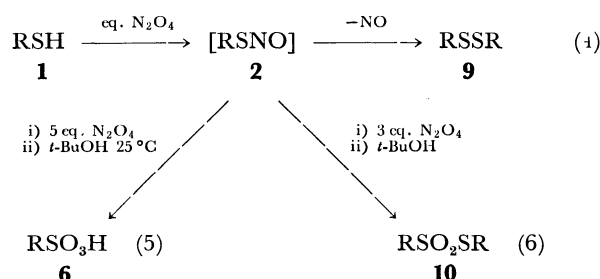
*Chemical Reactivities and Synthetic Applications of Thionitrites.* Both aromatic and alkyl thiols (**1d**, **1j**, **1k**, **1l**, **1e**, **1g**, **1h**, and **1i**) reacted readily with excess

TABLE 4. <sup>1</sup>H-NMR CHEMICAL SHIFTS OF *t*-BUTYL GROUPS IN *O*- AND *S*-NITROSO OR NITRO COMPOUNDS

| Compound  | Chemical shift of <i>t</i> -butyl group (CCl <sub>4</sub> , ppm) |
|-----------|------------------------------------------------------------------|
| <b>7</b>  | 1.60                                                             |
| <b>8</b>  | 1.54                                                             |
| <b>2a</b> | 1.85                                                             |
| <b>3a</b> | 1.58                                                             |

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

| Compound  | Wavelength/nm (ε)                                    |
|-----------|------------------------------------------------------|
| <b>7</b>  | 196 (6700), 219 (3300), 339 (28), 351 (48), 397 (57) |
| <b>8</b>  | 201 (5200), 380 (87), 397 (57)                       |
| <b>2a</b> | 198 (5000), 228 (8600), 342 (630)                    |
| <b>3a</b> | 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**11**, **10e**: R = *o*-Tolyl**1e**, **10f**: R = *p*-Cl-C<sub>6</sub>H<sub>4</sub>**1g**, **10g**: R = *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>**1h**, **10h**: R = cyclohexyl**1i**, **10i**: R = *n*-C<sub>8</sub>H<sub>17</sub>

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<sup>6)</sup> or by the reaction of sulfinic acids with sulfonyl chlorides.<sup>7)</sup> 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 tetroxide at *ca.* −20–0 °C and then quenched with *t*-butyl alcohol, the corresponding thiosulfonic *S*-esters **10b–i** were obtained

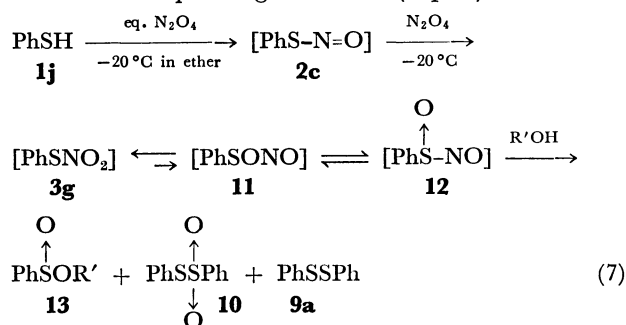
TABLE 6. REACTIONS OF THIOLS WITH DINITROGEN TETRAOXIDE

| Thiol     | Reaction time/min | Reaction temp/°C | $\frac{[\text{N}_2\text{O}_4]^a}{[\text{RSH}]}$ | Product    | Isolated yield/% |
|-----------|-------------------|------------------|-------------------------------------------------|------------|------------------|
| <b>1a</b> | 5                 | 25               | 4                                               | <b>3a</b>  | 87               |
| <b>1d</b> | 5                 | -20              | 4                                               | <b>10b</b> | 65               |
| <b>1j</b> | 5                 | -20              | 4                                               | <b>10c</b> | 88               |
| <b>1k</b> | 1                 | 0                | 4                                               | <b>10d</b> | 65               |
| <b>1l</b> | 1                 | 0                | 4                                               | <b>10e</b> | 77               |
| <b>1e</b> | 5                 | -20              | 4                                               | <b>10f</b> | 77               |
| <b>1g</b> | 1                 | 0                | 4                                               | <b>10g</b> | 70               |
| <b>1h</b> | 5                 | -20              | 4                                               | <b>10h</b> | 62               |
| <b>1i</b> | 1                 | 0                | 4                                               | <b>10i</b> | 60               |
| <b>1j</b> | 3                 | -70              | 1                                               | <b>9a</b>  | ca. 100          |
| <b>1j</b> | 120               | 25               | 6                                               | <b>6a</b>  | ca. 100          |
| <b>1d</b> | 120               | 25               | 6                                               | <b>6b</b>  | ca. 100          |

a) Mole ratio.

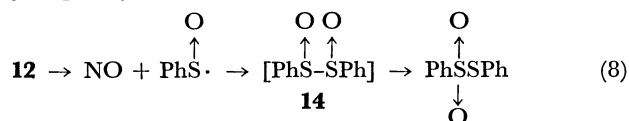
in good yields in such an inert solvent as ethyl ether. A solution of dinitrogen tetraoxide (in  $\text{CCl}_4$ ) was added to a solution of a certain thiol in anhydrous ethyl ether at ca.  $-20^\circ\text{C}$ . Immediately, the mixture colored to bright red, characteristic of thionitrite **2**, which 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.  $-20^\circ\text{C}$  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,

**13a:** R' = Me**13b:** R' = Me<sub>2</sub>CH

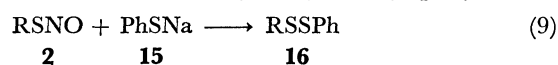
bulky *t*-butyl alcohol may not attack the sulfinyl sulfur atom due to the steric hindrance. When the reaction mixture was quenched with *t*-butyl alcohol, *t*-butyl benzenesulfinate could not be detected. Probably, homolytic scission of the unstable intermediate **12** may form the sulfinyl radical which is con-

verted to the corresponding diphenyl  $\alpha$ -disulfoxide (**14**), which then would be converted to the corresponding *S*-phenyl benzenethiosulfonate (**10c**)<sup>8,9</sup> (Eq. 8).

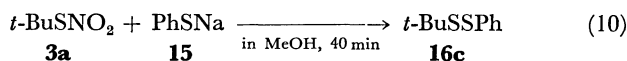


Meanwhile treatment of the thiol **1d**, and **1j** with 6 eq. dinitrogen tetraoxide at room temperature followed by quenching with excess *t*-BuOH gave the sulfonic acids (**6a,b**) quantitatively (Eq. 5), whereas treatment of thiol **1j** with 1 eq. with dinitrogen tetraoxide at  $-70^\circ\text{C}$  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.<sup>2)</sup> 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).

**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 benzenethiolate **15** at room temperature to afford *t*-butyl phenyl disulfide (**16c**) in 69% isolated yield (Eq. 10).

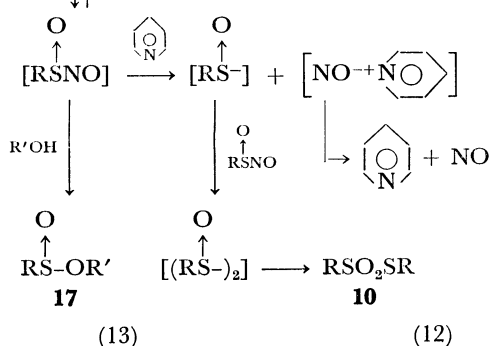
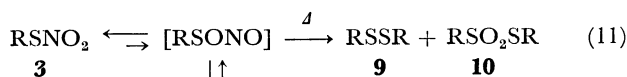


When thionitrate **3a** was heated in carbon tetrachloride for 1 h at  $130^\circ\text{C}$  in a sealed tube, di-*t*-butyl disulfide (**9c**) was obtained as the major product, whereas decomposition of thionitrate **3d** at room temperature gave thiosulfonic *S*-ester **10b** as the main product together 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% yield (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).

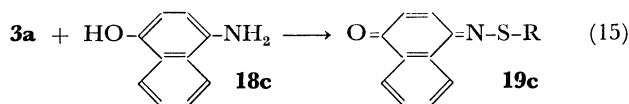
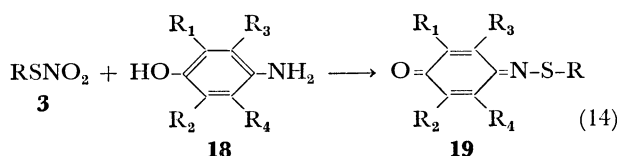
Only a few *N*-(alkylthio)-*p*-benzoquinone imines were prepared previously from *N*-chloro-*p*-benzoquinone imines and thiols.<sup>10)</sup> Our new synthetic

method of quinone imines **19a—i** is simple and especially useful for the syntheses of *N*-*t*-alkylthio derivatives.



**3a, 9c, 10j:** R = *t*-Bu  
**3d, 9b, 10b:** R = *p*-Tolyl

**3e, 10k:** R = *t*-C<sub>5</sub>H<sub>11</sub>  
**17:** R = *p*-Tolyl, R' = CH<sub>3</sub>



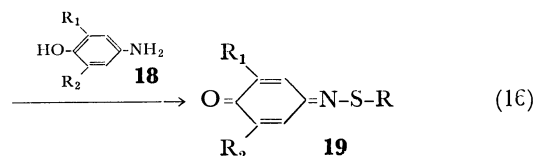
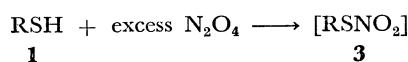
**18a, 19a:** R = *t*-Bu, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
**18b, 19b:** R = *t*-Bu, R<sub>3</sub> = CH<sub>3</sub>, R<sub>1</sub> = R<sub>2</sub> = R<sub>4</sub> = H  
**18d, 19d:** R = *t*-Bu, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = R<sub>4</sub> = H  
**18e, 19e:** R = *t*-Bu, R<sub>1</sub> = R<sub>2</sub> = Cl, R<sub>3</sub> = R<sub>4</sub> = H  
**18f, 19f:** R = *t*-C<sub>5</sub>H<sub>11</sub>, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
**18g, 19g:** R = 1,1-dimethylheptyl, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
**18h, 19h:** R = *p*-Cl-C<sub>6</sub>H<sub>4</sub>, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
**18i, 19i:** R = *p*-Br-C<sub>6</sub>H<sub>4</sub>, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H

TABLE 7. REACTIONS OF THIONITRATES WITH AMINOPHENOLS

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

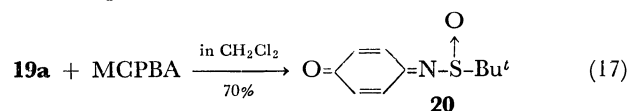
a) In this case CuCl<sub>2</sub> was not added. Chromatographic separation gave a poor result and the yield was determined by GLC. b) HCl salt was used as the starting material. c) An oxidative mixture of the thiol with 2 eq. N<sub>2</sub>O<sub>4</sub> was used due to the instabilities of these thionitrates. d) CuCl<sub>2</sub> was not used in these cases for instabilities of these thionitrates in the presence of CuCl<sub>2</sub>.

An oxidative mixture of *s*-BuSH (**1m**) or thiol **1d** with excess dinitrogen tetroxide 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 ( $\epsilon_{\text{max}} > 10^4$ ) near 400 nm. Structures of the products **19a—k** were identified by IR, NMR, UV, and mass spectroscopies. Elemental analyses of these compounds **19a—k** all agree with these formulae. Isolated yields of compounds **19a—k** are listed in Table 7.

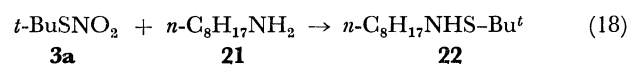


**1m, 3h:** R = *s*-Bu  
**1d, 3d:** R = *p*-Tolyl  
**18j, 19j:** R = *s*-Bu, R<sub>1</sub> = R<sub>2</sub> = Cl  
**18k, 19k:** R = *p*-Tolyl, R<sub>1</sub> = R<sub>2</sub> = H

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<sup>-1</sup> (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).



**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*-TolSO<sub>2</sub>)<sub>3</sub>(NO) (**23**)<sup>11)</sup> 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.<sup>3)</sup> Other several sulfonyl nitrites **5a, 5c, 5d**, and **5e** were also found to undergo thermodecomposition to give white crystals described as formula (RSO<sub>2</sub>)<sub>3</sub>(NO) (**23a, 23c—e**) by elemental analyses (Eq. 19). However, since the compound **23a** gives two distinctly different peaks of methyl groups on both <sup>1</sup>H and <sup>13</sup>C-NMR spectra (integral ratio = 2:1 on <sup>1</sup>H-NMR), the structure of these compounds **23a—e**



TABLE 9. SPECTROSCOPIC DATA AND MELTING POINTS OF THIONITRATES

| Thionitrate | IR (neat, cm <sup>-1</sup> )      | NMR (CCl <sub>4</sub> , ppm)                                                                                             |
|-------------|-----------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| <b>3a</b>   | 1510, 1300, 1263, 1155, 820       | 1.58 (s)                                                                                                                 |
| <b>3b</b>   | 1510, 1300, 1255, 1150, 821       | 1.00 (t, 3H, -CH <sub>2</sub> CH <sub>3</sub> ),<br>1.33 (s, 6H, -CH <sub>3</sub> ),<br>1.70 (q, 2H, -CH <sub>2</sub> -) |
| <b>3c</b>   | 1510, 1297, 1250, 1130, 813       | 0.73—2.33 (m, 11H),<br>1.45 (t, 2H, CH <sub>2</sub> CS),<br>1.55 (s, 6H, CH <sub>3</sub> )                               |
| <b>3d</b>   | 1510, 1378, 1290, 800             | Mp 32—33 °C (dec)                                                                                                        |
| <b>3e</b>   | 1510, 1378, 1300, 1070, 1000, 810 | Mp 44—45 °C (dec)                                                                                                        |
| <b>3f</b>   | 1510, 1375, 1290, 1055, 1000, 812 | Mp 49—50 °C (dec)                                                                                                        |

TABLE 10. ELEMENTAL ANALYSES AND BOILING POINTS OF STABLE THIONITRATES

| Thio-nitrate | Found (%) |      |      | Calcd (%) |      |      | Bp (°C/mmHg)                           |
|--------------|-----------|------|------|-----------|------|------|----------------------------------------|
|              | C         | H    | N    | C         | H    | N    |                                        |
| <b>3a</b>    | —         | —    | —    | —         | —    | —    | 40—41/6<br>(lit, <sup>17</sup> ) 55/13 |
| <b>3b</b>    | 40.05     | 7.29 | 9.01 | 40.24     | 7.43 | 9.38 | 36—38/3                                |
| <b>3c</b>    | 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 <sup>-1</sup> ) |                   | NMR (CDCl <sub>3</sub> , ppm) |                                                              |
|------------------|-----------------------------|-------------------|-------------------------------|--------------------------------------------------------------|
|                  | NO                          | SO <sub>2</sub>   | CH <sub>3</sub>               | Ring proton                                                  |
| <b>5a</b>        | 1842                        | 1355<br>1157      | 3.36 (br, s)                  |                                                              |
| <b>5b</b>        | 1850                        | 1390<br>1185      | 2.37 (s, 3H)                  | 7.10 (d, <i>J</i> =8 Hz, 2H)<br>7.50 (d, <i>J</i> =8 Hz, 2H) |
| <b>5c</b>        | 1860                        | 1390<br>1840 1190 |                               | 7.21—7.85 (m, 4H)                                            |
| <b>5d</b>        | 1859                        | 1398              |                               | 7.39 (d, <i>J</i> =10 Hz, 2H)                                |
|                  | 1835                        | 1195              |                               | 7.68 (d, <i>J</i> =10 Hz, 2H)                                |
| <b>5e</b>        | 1858                        | 1390<br>1835 1191 |                               | 7.65 (br, m)                                                 |
| <b>5f</b>        | 1880                        | 1382              | 3.90 (s, 3H)                  | 6.80—7.15 (m, 2H)                                            |
|                  | 1860                        | 1195              |                               | 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 tetroxide (20 mmol, in CCl<sub>4</sub>) 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**<sup>a)</sup>

| Compound  | Found (%) <sup>b)</sup> |      |      |       | Calcd (%) |      |      |       |
|-----------|-------------------------|------|------|-------|-----------|------|------|-------|
|           | C                       | H    | N    | S     | C         | H    | N    | S     |
| <b>5b</b> | 45.43                   | 3.76 | 7.37 | 17.16 | 45.39     | 3.80 | 7.56 | 17.31 |
| <b>5c</b> | 42.40                   | 2.89 | 7.68 | 18.59 | 42.10     | 2.94 | 8.18 | 18.73 |
| <b>5d</b> | 35.43                   | 1.97 | 6.36 | 15.73 | 35.04     | 1.96 | 6.81 | 15.59 |
| <b>5e</b> | 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 <sup>-1</sup> ) |                     | NMR (CCl <sub>4</sub> , ppm)                           | Mp/°C                                       |
|------------|------------------------|---------------------|--------------------------------------------------------|---------------------------------------------|
|            | asym SO <sub>2</sub>   | sym SO <sub>2</sub> |                                                        |                                             |
| <b>10b</b> | 1320                   | 1137                | 2.33 (s, 6H)<br>6.9—7.5 (m, 8H)                        | 76—78<br>(lit, <sup>19</sup> ) 78.5—79.5    |
| <b>10c</b> | 1325                   | 1143                | 7.0—7.7 (m)                                            | 44—45<br>(lit, <sup>18</sup> ) 45)          |
| <b>10d</b> | 1325                   | 1138                | 2.26 (s, 3H)<br>2.27 (s, 3H)<br>6.9—7.5 (m, 8H)        | Oil<br>(lit, <sup>20</sup> ) Oil)           |
| <b>10e</b> | 1321                   | 1143                | 2.16 (s, 3H)<br>2.63 (s, 3H)<br>6.9—7.5 (m, 8H)        | 52—54<br>(lit, <sup>18</sup> ) 55—56)       |
| <b>10f</b> | 1323                   | 1139                | 7.2—7.5 (m)                                            | 135—136<br>(lit, <sup>21</sup> ) 138)       |
| <b>10g</b> | 1343                   | 1142                | 7.3—8.5                                                | 176—178<br>(lit, <sup>22</sup> ) 180—180.5) |
| <b>10h</b> | 1332                   | 1135                | 0.7—2.5 (m, 20H)<br>2.9 (br, m, 1H)<br>3.3 (br, m, 1H) | Oil<br>(lit, <sup>23</sup> ) 37—38)         |
| <b>10i</b> | 1325                   | 1129                | 0.7—2.1 (m, 30H)<br>2.9—3.3 (m, 4H)                    | Oil<br>(lit, <sup>24</sup> ) 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<sub>3</sub> 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 tetroxide (15 mmol, in CCl<sub>4</sub>) 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 tetroxide (5

mmol, in  $\text{CCl}_4$ ) was added to a stirred solution of thiol **1j** (550 mg, 5 mmol) in dry ethyl ether (10 ml) at  $-70^\circ\text{C}$ . After a few minutes the red colored solution was poured into the 5%  $\text{NaHCO}_3$  aq solution. After the mixture was warmed to room temperature. After the red color of the thionitrite disappeared, the ethereal layer was separated, dried ( $\text{MgSO}_4$ ) 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  $\text{CCl}_4$ ) was added to a solution of thiol **1j** (421 mg, 3.8 mmol) at  $-20^\circ\text{C}$ . After a few minutes, the solution was quenched with methanol (1.2 ml) and stirred further for 5 min at  $0^\circ\text{C}$ . After evaporation of the solvent and TLC (hexane:ether=10:1) gave 65 mg (22%) of sulfinate **13a**: bp (bath temp)  $90-100^\circ\text{C}/2$  mmHg (lit.<sup>25</sup>  $76-81^\circ\text{C}/0.45$  mmHg). IR (neat): 1130 (SO), 965, 758, and  $696\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ):  $\delta=3.33$  (s, 3H,  $-\text{CH}_3$ ) 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)  $120-130^\circ\text{C}/2$  mmHg (lit.<sup>26</sup>  $110-117^\circ\text{C}/0.5$  mmHg). IR (neat): 1143 (SO), 1102, 920, 845, and  $735\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ):  $\delta=1.13$  (d,  $J=6$  Hz, 3H,  $-\text{CH}_3$ ), 1.34 (d,  $J=6$  Hz, 3H,  $-\text{CH}_3$ ), 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  $\text{CCl}_4$ ) was added to a stirred solution of thiol **1d** (620 mg, 5 mmol) in 10 ml of ethyl ether at  $-70^\circ\text{C}$ . After a few minutes, 5% aq  $\text{NaHCO}_3$  solution was added and extracted with 10 ml of ethyl ether. The ethereal solution was dried ( $\text{MgSO}_4$ ) and filtered at  $0^\circ\text{C}$ . 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  $-10^\circ\text{C}$ . The solution was washed with  $\text{NaHCO}_3$  aq solution and dried ( $\text{MgSO}_4$ ). 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  $130^\circ\text{C}$  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  $22-24^\circ\text{C}$ , bp (bath temp)  $80^\circ\text{C}/5$  mmHg. IR (neat): 1445, 1360, 1290 ( $\text{SO}_2$ ), 1140, and  $1100\text{ cm}^{-1}$  ( $\text{SO}_2$ ). NMR ( $\text{CCl}_4$ ):  $\delta=1.40$  and 1.58. MS (70 eV),  $m/e$  (rel intensity), 210 (1,  $\text{M}^+$ ), 89 (10, *t*-BuS<sup>+</sup>), and 57 (100, *t*-Bu<sup>+</sup>). Found:

C, 45.59; H, 8.61; S, 30.29%. Calcd for  $\text{C}_8\text{H}_{18}\text{O}_2\text{S}_2$ : C, 45.68; H, 8.62; S, 30.48%.

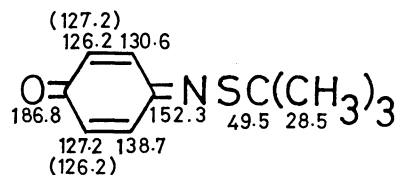
Thiosulfonic *S*-ester **10b** (65%) and thiosulfonic *S*-ester **10k** (89%) were obtained from thionitrate **3d** and thionitrate **3c**, respectively. IR spectroscopic data of thiosulfonic *S*-ester **10b** were identical with those of authentic sample. Thiosulfonic *S*-ester **10k**: bp (bath temp)  $80^\circ\text{C}/3$  mmHg. IR (neat): 1455, 1295, and  $1100\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ):  $\delta=1.00$  (t, 6H,  $\text{CH}_2-\text{CH}_3$ ), 1.35 (s, 6H,  $\text{SC}(\text{CH}_3)_2$ ), and 1.88 (q, 4H,  $\text{CH}_2$ ). Found: C, 50.39; H, 9.43%. Calcd for  $\text{C}_{10}\text{H}_{22}\text{O}_2\text{S}_2$ : 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  $-20^\circ\text{C}$ . 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,  $\text{M}^+$ ), 139 (100, *p*-TolSO<sub>2</sub><sup>+</sup>), and 91 (28, *p*-Tol<sup>+</sup>). IR and NMR spectroscopic data were identical with those of literatures.<sup>27</sup> 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 ( $\text{MgSO}_4$ ) 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 <sup>13</sup>C-NMR spectrum (in  $\text{CDCl}_3$ , 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  $0^\circ\text{C}$ . 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<sup>28</sup> and the filtrate was diluted with ethyl ether, washed with aq  $\text{NaHCO}_3$  solution, dried ( $\text{MgSO}_4$ ), evaporated and the usual TLC separation

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

| Com-<br>pound | UV<br>(hexane, $\lambda_{\max}$ , nm) | IR<br>( $\nu_{\text{C=O}}$ , $\text{cm}^{-1}$ ) | Found (%) |      |      |       | Calcd (%) |      |      |       |
|---------------|---------------------------------------|-------------------------------------------------|-----------|------|------|-------|-----------|------|------|-------|
|               |                                       |                                                 | C         | H    | N    | S     | C         | H    | N    | S     |
| <b>19a</b>    | 401 ( $\epsilon=2.7 \times 10^4$ )    | 1630                                            | 61.38     | 6.60 | 7.13 | 16.29 | 61.51     | 6.71 | 7.17 | 16.42 |
| <b>19b</b>    | 399 ( $\epsilon=2.1 \times 10^4$ )    | 1630                                            | 63.48     | 7.29 | 6.70 | 15.36 | 63.12     | 7.22 | 6.69 | 15.32 |
| <b>19c</b>    | 418 ( $\epsilon=1.9 \times 10^4$ )    | 1642                                            | 68.53     | 6.16 | 5.70 | 12.90 | 68.54     | 6.14 | 5.78 | 13.07 |
| <b>19d</b>    | 405 ( $\epsilon=2.4 \times 10^4$ )    | 1615                                            | 64.29     | 7.43 | 6.09 | —     | 64.53     | 7.67 | 6.27 | —     |
| <b>19e</b>    | 424 ( $\epsilon=3.4 \times 10^4$ )    | 1648                                            | 45.83     | 4.16 | 5.32 | —     | 45.46     | 4.19 | 5.30 | —     |
| <b>19f</b>    | 402 ( $\epsilon=2.7 \times 10^4$ )    | 1632                                            | 62.93     | 7.08 | 6.34 | —     | 63.12     | 7.22 | 6.69 | —     |
| <b>19g</b>    | 405 ( $\epsilon=2.7 \times 10^4$ )    | 1630                                            | 67.54     | 8.73 | 4.99 | —     | 67.88     | 8.73 | 5.27 | —     |
| <b>19h</b>    | 447 ( $\epsilon=2.2 \times 10^4$ )    | 1620                                            | 58.00     | 3.16 | 5.39 | —     | 57.71     | 3.22 | 5.60 | —     |
| <b>19i</b>    | 448 ( $\epsilon=2.1 \times 10^4$ )    | 1630                                            | 48.60     | 2.59 | 4.37 | —     | 48.99     | 2.74 | 4.76 | —     |
| <b>19j</b>    | 425 ( $\epsilon=2.2 \times 10^4$ )    | 1645                                            | 45.68     | 4.20 | 5.41 | —     | 45.46     | 4.19 | 5.30 | —     |
| <b>19k</b>    | 438 ( $\epsilon=1.7 \times 10^4$ )    | 1625                                            | 68.28     | 4.73 | 5.83 | —     | 68.09     | 4.83 | 6.10 | —     |

TABLE 15.  $^1\text{H}$ -NMR SPECTROSCOPIC DATA ( $\text{CCl}_4$ , ppm) OF QUINONE IMINE **19a–k**

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

a) Contains ring proton.

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

| Compound   | MS (70 eV), $m/e$ (rel intensity)           |
|------------|---------------------------------------------|
| <b>19a</b> | 195 (37, $\text{M}^+$ ), 138 (86), 57 (44)  |
| <b>19b</b> | 209 (28, $\text{M}^+$ ), 152 (44), 57 (100) |
| <b>19c</b> | 245 (22, $\text{M}^+$ ), 188 (100), 57 (84) |
| <b>19d</b> | 223 (44, $\text{M}^+$ ), 166 (100), 57 (61) |
| <b>19e</b> | 263 (48, $\text{M}^+$ ), 206 (77), 57 (100) |
| <b>19f</b> | 209 (31, $\text{M}^+$ ), 138 (100), 71 (50) |
| <b>19g</b> | 265 (9, $\text{M}^+$ ), 138 (100), 127 (11) |
| <b>19h</b> | 249 (100, $\text{M}^+$ ), 143 (73)          |
| <b>19i</b> | 294 (97, $\text{M}^+$ ), 188 (100)          |
| <b>19j</b> | 263 (41, $\text{M}^+$ ), 206 (69), 57 (100) |
| <b>19k</b> | 229 (100, $\text{M}^+$ ), 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  $\text{cm}^{-1}$  (SO). UV (hexane):  $\lambda_{\max}=415$  nm. NMR ( $\text{CCl}_4$ ):  $\delta=1.32$  (s, 9H, *t*-Bu), 6.48 (d,  $J=10$  Hz, 2H,  $\text{O}=\text{C}-\text{CH}$ ), and 6.93 (d,  $J=10$  Hz, 2H,  $\text{O}=\text{C}-\text{C}=\text{CH}$ ). MS (70 eV),  $m/e$  (rel intensity), 211 (1,  $\text{M}^+$ ), 154 (100,  $\text{O}=\text{C}=\text{CH}=\text{NSO}^+$ ), and 57 (17, *t*-Bu<sup>+</sup>). Sulfinyl derivative **20** was unstable at room temperature, and soon

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

| Compound   | IR (KBr, cm <sup>-1</sup> ) |                     | Mp/°C   |
|------------|-----------------------------|---------------------|---------|
|            | asym SO <sub>2</sub>        | sym SO <sub>2</sub> |         |
| <b>23a</b> | 1380                        | 1175                | 139—140 |
| <b>23b</b> | 1390                        | 1195                | 190—192 |
|            |                             | 1175                |         |
| <b>23c</b> | 1395                        | 1197                | 99—101  |
| <b>23d</b> | 1400                        | 1190                | 168—170 |
| <b>23e</b> | 1395                        | 1192                | 198—200 |

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

| Compound   | Found (%) |      |      | Calcd (%) |      |      |
|------------|-----------|------|------|-----------|------|------|
|            | C         | H    | N    | C         | H    | N    |
| <b>23a</b> | 13.57     | 3.23 | 5.14 | 13.48     | 3.39 | 5.24 |
| <b>23b</b> | 51.27     | 4.05 | 2.84 | 50.90     | 4.27 | 2.83 |
| <b>23c</b> | 47.49     | 3.24 | 2.76 | 47.67     | 3.33 | 3.09 |
| <b>23d</b> | 39.19     | 2.20 | 2.46 | 38.82     | 2.17 | 2.51 |
| <b>23e</b> | 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<sup>-1</sup>. NMR (CCl<sub>4</sub>): δ=0.6—2.0 (m, 15H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>-), 1.17 (s, 9H, *t*-Bu), 2.36 (br, 1H, NH), and 2.86 (br, 2H, -CH<sub>2</sub>-NH). Found: C, 65.95; H, 12.41; N, 6.32%. Calcd for C<sub>12</sub>H<sub>17</sub>NS: C, 66.29; H, 12.52; N, 6.44%. The other main product was *t*-BuSO<sub>2</sub>S-Bu<sup>t</sup> (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.<sup>3)</sup> 126 °C). IR (KBr): 3260 (OH), 1380 (SO<sub>2</sub>), 1190 (SO<sub>2</sub>), 855, and 673 cm<sup>-1</sup>. IR spectroscopic data were identical with those of authentic sample prepared by the method in the literature.<sup>3)</sup>

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.<sup>29</sup> 69 °C). IR (KBr): 1591, 1460, 1318, 1140, 811, and 702 cm<sup>-1</sup>. NMR (CCl<sub>4</sub>): δ=1.43 (s, 9H, *t*-Bu), 2.42 (s, 3H, CH<sub>3</sub>), 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<sup>+</sup>), 187 (9, *p*-TolSO<sub>2</sub>S<sup>+</sup>), 155 (10, *p*-TolSO<sub>2</sub><sup>+</sup>), 91 (27, *p*-Tol<sup>+</sup>), 89 (5, *t*-BuS<sup>+</sup>), and 57 (100, *t*-Bu<sup>+</sup>).

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<sub>4</sub>), 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<sub>2</sub>), 985, 815, and 730 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): δ=2.45 (s, 3H, -CH<sub>3</sub>), 3.88 (br, 2H, NH and OH), 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<sub>7</sub>H<sub>9</sub>NO<sub>3</sub>S: C, 44.90; H, 4.84; N, 7.48%.

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