New Syntheses of Thionitrites and their Chemical Reactivities [1]

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Both aryl and alkyl thionitrites (RSNO) were prepared quantitatively by the reaction of thiols with dinitrogen tetraoxide (N_2O_4) under mild conditions. Unstable thionitrites were identified by i.r. or u.v. spectra at low temperatures (*e.g.* 0 °C) or by their further reactions with nucleophiles leading to known derivatives. The spectroscopic data of these thionitrites are summarized and the highly reactive thionitrites were found to react readily with other nucleophiles such as thiols, sulphinic acids, alcohols, and secondary amines at *ca.* −5 °C. Treatment of thionitrites with other thiols or sulphinic acids was found to yield the corresponding unsymmetrical disulphides or thiolsulphonates in good yields. Similar treatment of thionitrites with secondary amines or alcohols gave the corresponding *N*-nitrosoamines, or disulphides and nitrites.

A FEW stable alkyl thionitrites (RSNO) have been prepared by treating alkanethiols with either alkyl nitriles,[2] nitrosyl chloride,[3] or nitrous anhydride.[4] A few attempts to prepare aryl thionitrites have also been made, though unsuccessfully.[3,5] Since alkyl thionitrites of low molecular weight were characterized mainly by i.r. spectroscopic analysis in the gas phase due mainly to their instability, the yields and purities of these thionitrites were not reliable because of their ready decomposition. Recently we found that both arene- and alkane-thiols react readily with an equimolar amount of dinitrogen tetraoxide (N_2O_4) under mild conditions (−10 to 0 °C) affording the corresponding thionitrites quantitatively.[1a] The highly reactive thionitrites were found to react immediately with other thiols or sulphinic acids affording the corresponding unsymmetrical di-sulphides (3) or thiolsulphonates (4) in good yield. In contrast, the reaction of thionitrites with alcohols is slow and yields the corresponding disulphides and alkyl nitrites. The reaction with amines is also slow and gives nitroso-compounds (6). This paper describes the synthesis of both aryl and alkyl thionitrites and a few typical reactions with nucleophiles such as thiols, sulphinic acids, and secondary amines and alcohols. These reactions are illustrated in Scheme 1.

Preparation of Thionitrites.—The reaction of thiols with N_2O_4 in an inert solvent such as CCl_4, hexane, ether, or acetonitrile yields the corresponding thionitrites quantitatively, if an equivalent amount of N_2O_4 was used and the temperature was kept sufficiently low, *i.e.* below −10 °C. N_2O_4 is known to be in an equilibrium with NO^+ and NO_3^- ion [6]. Probably electrophilic attack of NO^+ on the sulphur atom of the thiol forms the corresponding thionitrite and nitric acid. The yields are quantitative and hence remarkably high by comparison with those for the known reactions of thiols with either alkyl nitrite,[2] nitrosyl chloride,[3] or nitrous anhydride.[4]

Characterization of Thionitrites.—The spectra and

yields of alkyl and aryl thionitrites prepared by treating the corresponding thiols with N_2O_4 are summarized in Table 1. The characteristic broad, strong i.r. band at 1 500—1 550 cm⁻¹ has been assigned to the stretching vibration of the nitroso group of the thionitrite†. A more convenient and reliable identification of the thionitrite is provided by the typical visible spectra, $\lambda_{max.}$ 515 and 550 nm for the red n-alkyl thionitrites, $\lambda_{max.}$ 552, 562, 598, and 605 nm for the red-green t-butyl thionitrite,‡ $\lambda_{max.}$ 530 and 570 nm for the dark red aromatic thionitrites. The visible absorption for benzyl [8] and α-phenethyl thionitrite are in the middle region between those of n-alkyl and aryl thionitrites.
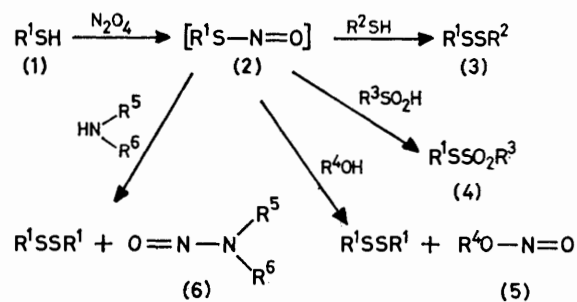
SCHEME 1

Stability of Thionitrites.—In the reaction of the thiol with N_2O_4 in CCl_4 the maximum yield of the thionitrite was achieved when an equivalent amount of N_2O_4 for the thiol was added. However, if any excess N_2O_4 was used, the yield of the thionitrite decreased (Figure 1). This was also the case for phenyl (at *ca.* 0 °C), benzyl (at *ca.* 20 °C), and n-octyl (at *ca.* 20 °C) thionitrites [Figure (1B)]. In contrast to these thionitrites, t-butyl thionitrite is stable under the same conditions [Figure (1A)]. The remarkably stable t-butyl thionitrite is known to be oxidized further to the thionitrate [(CH_3)$_3CSNO_2$] by N_2O_4 or HNO_3 at 60 °C.[9,10] However, the characteristic

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† The gas-phase i.r. spectra of methyl and ethyl thionitrites showed $\nu_{max.}$ 1 962 (−S−N=O), 1 534 (−N=O), and 730 cm⁻¹ (C−S).[4]

‡ The electronic spectra for heptane–ethanol has been published,[7] $\lambda_{max.}$ 340 (ε 990) and 599 nm (15.5).

[1] (a) S. Oae, D. Fukushima, and Y. H. Kim, *J.C.S. Chem. Comm.,* 1977, 407; (b) S. Oae, Y. H. Kim, D. Fukushima, and T. Takata, *Chem. Letters,* 1977, 893.

[2] H. Lecher and W. Siefhen, *Ber.,* 1926, **59,** 1314, 2594.

[3] H. S. Tasker and H. O. Jones, *J. Chem. Soc.,* 1909, **95,** 1910.

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[5] H. Reinboldt, *Ber.,* 1926, **59,** 1311.

[6] P. Gray and A. D. Yoffe, *Quart. Rev.,* 1955, **9,** 376.

[7] G. Kresze and U. Uhlich, *Chem. Ber.,* 1959, **92,** 1048.

[8] J. Barrett, D. F. Debenham, and J. Glouster, *Chem. Comm.,* 1965, 248.

[9] (a) H. Reinboldt and F. Mott, *Ber.,* 1932, **65,** 1223; (b) R. S. George, Amer. P., 1943, 2,307,624 (*Chem. Abs.,* 1943, **37,** 3588).

[10] K. Shinhama, D. Fukushima, Y. H. Kim, and S. Oae, unpublished data.

i.r. absorption bands of the thionitrate, 1 304 and 1 257 cm⁻¹,[7] could not be observed under this condition (at *ca.* 20 °C). t-Butyl thionitrite does not appear to be readily oxidized by excess of N_2O_4 at 20 °C, because of the

Decomposition of aromatic thionitrites appears to be accelerated by nitric acid formed during the reaction as is also the case for the alkyl nitrites.[11] In fact, thionitrites are quite unstable in the presence of nitric acid.

TABLE 1

Yields and spectra of thionitrites RSNO

R	Yield (%)	$\nu_{max.}/cm^{-1}$ [a]	$\lambda_{max.}/nm$ (ε) [b]
$CH_3(CH_2)_3$	*ca.* 100 [d]	1 910, 1 500—1 530	342 (780), 519 (13), 550 (27)
$(CH_3)_3C$ [e]	*ca.* 100 [d]	1 930, 1 490—1 520	345 (675), 562 (7), 552 (6), 598 (17), 605 (16)
$CH_3[CH_2]_9$	*ca.* 100 [d]	1 910, 1 500—1 530	339 (*ca.* 700), 515 (12), 547 (20)
$CH_3[CH_2]_7$	*ca.* 100 [d]	1 910, 1 510—1 520	339 (*ca.* 700), 515 (8), 547 (17)
CH_3CH_2	*ca.* 100 [d]	1 965, 1 910, 1 510—1 520	338 ( ),[e] 518 ( ),[e] 550 ( ) [e]
$PhCH_2$ [f]	*ca.* 96 [d]	1 600, 1 500—1 530	340 (1 020), 530sh (*ca.* 17), 560 (26)
$PhC(CH_3)H$	72 [g]	1 628, 1 495	341 (1 000), 520sh (*ca.* 20), 555 (41)
Ph [h]	97 [i]	1 900—1 910, 1 580—1 670	261 ( ),[j] 380 ( ),[j] 530 (27), 570 (42)
p-$CH_3C_6H_4$ [h]	91 [i]	1 910, 1 550—1 600	261 ( ),[j] 380 ( ),[j] 533 (26), 574 (51)
p-ClC_6H_4 [h]		1 880—1 910, 1 540—1 590	526 (26), 566 (53)

[a] In CCl_4 at 0 °C. [b] In hexane–CCl_4 (100:1) at 0 °C. [c] For ¹H n.m.r. (CCl_4) see Experimental section. [d] From h.p.l.c. (no side product obtained). [e] Ethyl thionitrite was too volatile to obtain the ε value. [f] U.v. spectrum already known,[8] $\lambda_{max.}$ (hexane) 340 (ε 1 030), 530sh, and 560 nm (26). [g] The yield was calculated from the n.m.r. spectrum of a concentrated sample, where the side product was only disulphide. [h] Since aromatic thionitrites are not stable during u.v. measurements even at −2 to 0 °C, the extinction coefficients should be more than those observed. [i] Yields were determined from the yield of the unsymmetrical disulphides obtained from reaction of the thionitrites and another thiols. [j] Good reproducibility could not be obtained.

steric hindrance of the tertiary alkyl groups. Most of the thionitrites decompose to give the corresponding disulphides when the reaction mixtures were concentrated without washing with a dilute alkali solution.

FIGURE 1 Yield of thionitrite as a function of $[N_2O_4]/[RSH]$ ratio. U.v. measurements were carried out at 20 °C soon after mixing thiols and N_2O_4 solution at −10 °C. The most intense u.v. peak for the thionitrites was observed for $[N_2O_4]/[RSH]$ 1.0 and was taken as the maximum relative intensity (1.0). ○, t-Butyl thionitrite in (A); ○, phenyl thionitrite in (B); ●, benzyl thionitrite in (B); △, n-octyl thionitrite in (B)

Unstable aromatic thionitrites can be obtained similarly and kept stable for *ca.* 20 min at 0 °C in argon.

α-Phenethyl thionitrite was purified and its stability to light and acids was examined (Table 2). While the decomposition of α-phenethyl thionitrite is slow under argon, the sulphur–nitrogen bond of the thionitrite is weak (calculated dissociation energy 52 kcal mol⁻¹) and undergoes homolytic fission under 365 nm radiation.[8]
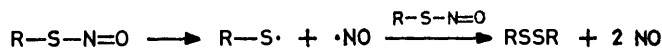
Decomposition of thionitrites gives nitric oxide and the

TABLE 2

Stability of α-phenethyl thionitrite

Condition	$T/°C$	$t_{1/2}/min$ [a]
No additive [b]	25	150
+ sun light	25	1.5
+ excess of N_2O_4 [c]	25	d
+ excess of N_2O_4 [c]	−10	1.5
+ conc. HNO_3 [e]	25	1.5
+ conc. H_2SO_4 [e]	25	12
+ NaOH [f]	25	60

[a] The disappearance of the absorption at 555 nm was measured. [b] 5 × 10⁻²M in CCl_4, open air in the dark. [c] Equal amount of N_2O_4 also added. [d] The decomposition was too fast to measure in these conditions (*ca.* 1 s). [e] A drop of acid was added and shaken vigorously. [f] Heterogeneous state.

corresponding disulphide, which is considered to be formed by the intermolecular reaction of the thionitrite with a thiyl radical formed by initial homolytic fission of the sulphur–nitrogen bond.[8] Decomposition of

$$R-S-N=O \longrightarrow R-S\cdot + \cdot NO \xrightarrow{R-S-N=O} RSSR + 2 NO$$

thionitrites is markedly faster in solution at higher than at lower concentrations.[1a] Aromatic thionitrites decompose rapidly in air, but are more stable under argon at −10 to 0 °C in the dark.

Reaction of Thionitrites with Other Thiols and Sulphinic Acids.—The thionitrites, either isolated or *in situ*, were allowed to react with other thiols or sulphinic acids to yield the corresponding unsymmetrical disulphides or thiolsulphonates in good yield. This is a one-pot

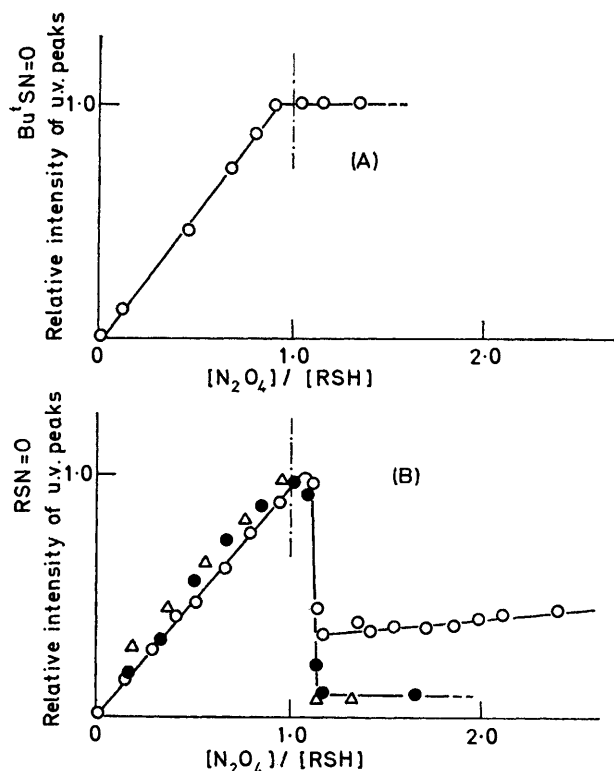[11] A. D. Allen, *J. Chem. Soc.*, 1954, 1968.

reaction in which the formation of byproducts by further oxidation is nearly negligible if an equimolar mixture of N_2O_4 and RSH is used to prepare the thionitrite. The results are summarized in Table 3.

If an equimolar mixture of N_2O_4 and R^1SH was used, R^1SH was converted completely into the thionitrite and hence when another thiol, R^2SH, was added, the yield of the unsymmetrical disulphide was remarkably high (runs 1, 3, 5, and 7). However, if the amount of N_2O_4 was 1.5-fold larger than that of R^1SH, the yield of the unsymmetrical disulphide, R^1–SS–R^2 decreased (runs 2, 4, 6, and 8). The yields were determined by g.l.c. using calibration curves from authentic samples.

TABLE 3
Yields of unsymmetrical disulphides and thiolsulphonates

Run	R^1	R^2	$[N_2O_4]/$ $[R^1SH]$	R^1SSR^2 (%)[a]	R^1SSR^1 (%)[a]
1	Ph	$(CH_3)_3C$	1	98[b]	1.2
2	Ph	$(CH_3)_3C$	1.5	70	1
3	Ph	$(CH_3)_2CH$	1	85	7
4	Ph	$(CH_3)_2CH$	1.5	66	1
5	Ph	$CH_3(CH_2)_7$	1	87	6
6	Ph	$CH_3(CH_2)_7$	1.5	55	9
7	Ph	p-$CH_3C_6H_4$	1	81	9
8	Ph	p-$CH_3C_6H_4$	1.5	21	
9	$(CH_3)_3C$	Ph	1	50	11
10	$(CH_3)_3C$	Ph	1.5	42	20
11	Ph	CH_3CH_2	1	81	9
12	CH_3CH_2	Ph	1	73	
13	p-$CH_3C_6H_4$	$(CH_3)_3C$	1	91[b]	1
14	$CH_3[CH_2]_7$	$CH_3(CH_2)_3$	1	81	6
15	$CH_3[CH_2]_7$	Ph	1.5	27	7

Run	R^1	R^3	$[N_2O_4]/$ $[R^1SH]$	$R^1SSO^2R^3$ (%)[b]	R^1SSR^1 (%)[b]
16	Ph	p-$CH_3C_6H_4$	1	80[c]	2
17	Ph	p-$CH_3C_6H_4$	1	74	5
18	p-$CH_3C_6H_4$	Ph	1	82	3
19	p-ClC_6H_4	Ph	1	73	12
20	$CH_3(CH_2)_3$	p-$CH_3C_6H_4$	1	61[c]	6

[a] Yields were determined by g.l.c. using calibration curves from authentic samples. [b] Isolated yields. [c] $[R^1SH]/[R^3SO_2H] = 1/1.5$

When t-butyl thionitrite was the substrate, the yield of $(CH_3)_3C$–SS–C_6H_5 was low (42—50%) regardless of the amount of N_2O_4, probably due to the steric hindrance of the three methyl groups. Even when $(CH_3)_3CSNO$ was treated with excess of N_2O_4 for 12 h at 5 °C, ca. 50% of the thionitrite was recovered.
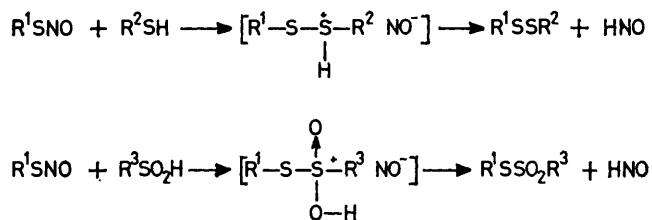
The formation of unsymmetrical disulphides and thiolsulphonates undoubtedly takes place via nucleophilic attack of the added thiols and sulphinic acids on the sulphur atom of the thionitrites (Scheme 2).*

Reaction of Thionitrites with Other Nucleophiles.— Thionitrites react with alcohols and secondary amines to yield O- and N-nitroso compounds though the yields of these products are rather low. Especially, a reaction with an amine such as piperidine is very slow and the yield is low. The reaction of alkali-washed n-butyl thionitrite with piperidine yielded 8.5% N-nitroso-piperidine and the corresponding n-butyl disulphide (19.5%) in 24 h at 25 °C and most of the thionitrate was recovered unchanged. When piperidine was added to a

* The presence of HNO was not confirmed in these reactions, but is known from similar reactions.[6]

solution of phenyl thionitrite prepared by treating thiophenol with a two-fold excess of N_2O_4 at -50 °C, N-nitrosopiperidine (85% from thiophenol) and a small amount of N-phenylsulphonylpiperidine ($<1\%$) were obtained.
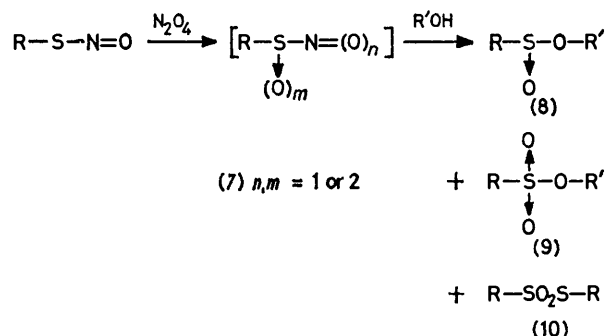
Similarly, the reaction of hexan-1-ol with phenyl thionitrite, yielded the corresponding hexyl nitrite

$$R^1SNO + R^2SH \longrightarrow \left[R^1-S-\overset{\cdot}{\underset{H}{S}}-R^2 \ NO^-\right] \longrightarrow R^1SSR^2 + HNO$$

$$R^1SNO + R^3SO_2H \longrightarrow \left[R^1-S-\overset{O}{\underset{O-H}{\overset{\uparrow}{S}}{}^{\cdot}-R^3} \ NO^-\right] \longrightarrow R^1SSO_2R^3 + HNO$$

SCHEME 2

(18%), diphenyl disulphide (70%), and recovered hexan-1-ol (64%). When the ratio r of N_2O_4 to thiophenol was <1.0 (r [N_2O_4] : [PhSH] 0.5—1.0), the reaction of the thionitrite with methanol afforded diphenyl disulphide (84%) and phenyl benzenethiolsulphonate (14%). However, when r was >1.0, phenyl benzenethiolsulphonate (41%), methyl benzenesulphinate (19%), and methyl benzenesulphonate (11%) were obtained. The relation between the yields of the products (disulphide, sulphinate, and sulphonate) and the time before quenching with methanol was shown in Figure 2.

The distribution of products, i.e. the disulphide and (8)—(10) did not change during 1 h from the beginning of the reaction at -10 to 0 °C [Figure (2B)]. However, at a low temperature (-30 to -50 °C), the distribution of the products changes depending on the quenching time [Figure (2A)]. If the thionitrite was quenched immediately with methanol at -30 to -50 °C, diphenyl disulphide was obtained quantitatively, suggesting strongly that the thionitrite is fairly stable in the presence of excess of N_2O_4 below -30 °C. However,

$$R-S-N=O \xrightarrow{N_2O_4} \left[R-S-N=(O)_n\right] \xrightarrow{R'OH} R-S-O-R'$$
$$\downarrow (O)_m \qquad\qquad \overset{O}{(8)}$$

$$(7) \ n,m = 1 \ or \ 2 \qquad + \ R-\overset{O}{\underset{O}{S}}-O-R'$$
$$(9)$$

$$+ \ R-SO_2S-R$$
$$(10)$$

above -10 °C, the thionitrite appears to be readily oxidized further by excess of N_2O_4 to an unstable intermediate such as (7) which reacts readily with methanol to give either the sulphinate (8) or the sulphonate (9). This esterification occurred even below -30 °C after more than 30 min in the presence of excess of N_2O_4 (Figure 2). n-Butyl thionitrite also reacted with methanol to yield the methyl esters of both the sulphinic

and the sulphonic acid as minor products (2—3%), when excess of N_2O_4 was used at 0 °C for 30 min. The mechanism of the formation of sulphinate (8), sulphonate (9), and thiolsuphonate (10) is not clear. However, the formation of the unstable intermediate (7) may be
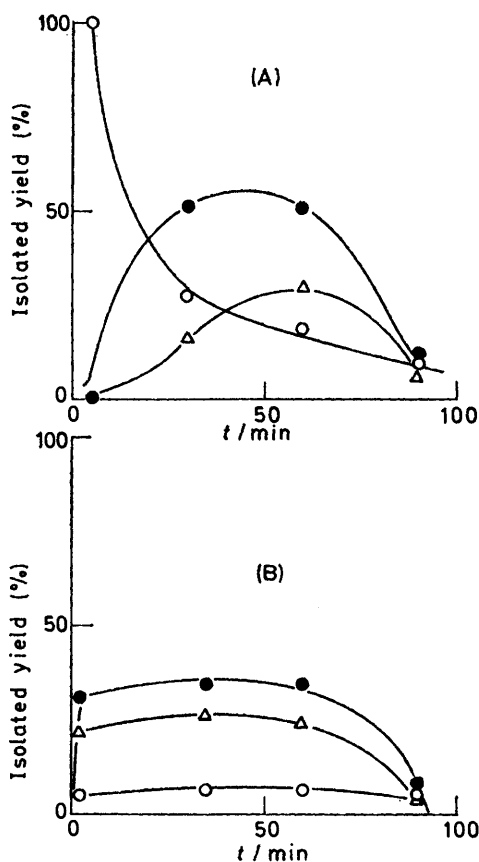

FIGURE 2 Relationship between yields of products and times before quenching: ○, PhSSPh; ●, PhSSO$_2$Ph; △, PhSO$_2$CH$_3$ +PhSO$_3$CH$_3$. All experiments were carried out at [N$_2$O$_4$]/ [PhSH] 2.5. Reaction temperatures are −30 to −50 °C for (A), 0 to −10 °C for (B)

considered as the initial step on the basis of product analysis.

EXPERIMENTAL

Preparation of N_2O_4–CCl_4 *Solution.*—NO$_2$ gas (Nippon Tokushu Gas Co.) was trapped in a cold flask containing P$_2$O$_5$ at *ca.* −20 °C. The trapped liquid N$_2$O$_4$ was again transferred, by warming at *ca.* 30 °C, into another flask containing P$_2$O$_5$ cooled at *ca.* −20 °C. The liquid N$_2$O$_4$ was finally distilled into precooled CCl$_4$ and used for further reaction.

Titration of N_2O_4–CCl_4 *Solution.*—The CCl$_4$ solution of N$_2$O$_4$ (0.1 ml) was quenched in cold water (10 ml) and then gradually warmed to *ca.* 20 °C. The nitric acid solution was titrated with 0.1N-NaOH. The concentration of N$_2$O$_4$ was calculated from the amount of NaOH used according to the stoicheiometric equation (1).[6,12]

Preparation of Thionitrites.—A solution of N$_2$O$_4$ (20 mmol) in CCl$_4$ (1 ml) at *ca.* −20 °C was added to a solution of a thiol (20 mmol) in ether or CCl$_4$ (50 ml) with vigorous stirring in the dark. Immediately the mixture became

$$3\ N_2O_4 + 2\ H_2O \longrightarrow 4\ HNO_3 + 2\ NO \qquad (1)$$
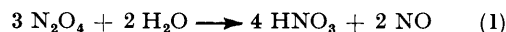
coloured. Relatively stable alkyl and α-phenethyl thionitrites were washed with 5% cold, aqueous sodium hydrogencarbonate solution and then with water to remove nitric acid formed during the reaction. The organic layer was separated and dried (MgSO$_4$). In the case of unstable aryl thionitrites, the same treatment was performed in the cold (*ca.* −2 °C). Alkyl thionitrites were distilled *in vacuo* at low temperature in the dark. All the thionitrites were prepared at *ca.* −2 °C. The purities of the alkyl thionitrites were checked by h.p.l.c. (Yanako L-1030 column, 0.2 × 50 cm; Gel-5510; carrier, methanol or acetonitrile) and n.m.r. (Hitachi R-24A). The side products, disulphides, derived from the decomposition of the thionitrites could not be observed. The purities and yields of unstable aryl thionitrites were determined from the yields of the unsymmetrical disulphides obtained in the reaction of the thionitrites and other thiols (Table 1).

Stabilities of Thionitrites.—A standard solution of PhSH (1.93 × 10⁻²M) in CCl$_4$ (100 ml) was divided into 5 ml portions which were then cooled to *ca.* −10 °C. Each portion was reacted with N$_2$O$_4$ solutions of different concentrations (8.75 × 10⁻³—1.75 × 10⁻¹ mmol) in CCl$_4$ (5— 100 μl). The intensities of the 254 nm peaks of the thionitrites were measured by h.p.l.c. Other thionitrites, $(CH_3)_3CSNO$ (thiol 3.12 × 10⁻¹M), $CH_3(CH_2)_7SNO$ (thiol 2.01 × 10⁻¹M), and PhCH$_2$SNO (thiol 4.99 × 10⁻²M), were similarly treated. The results are shown in Figure 1.

Measurements of I.r., N.m.r., and Electronic Spectra.— Unstable thionitrites were prepared at −2 °C and directly subjected to i.r. (Hitachi 215; CCl$_4$) and u.v. [JASCO UVIDEC-1; hexane–CCl$_4$ (100 : 1)] (Table 1) analysis. N.m.r. spectra of the comparatively stable t-butyl and α-phenethyl thionitrites were taken in CCl$_4$: t-butyl thionitrite, δ 1.87 (3 H, s); α-phenethyl thionitrite, δ 1.67 (3 H, d, *J* 7 Hz), 5.27 (1 H, q), and 7.18br (5 H).

Syntheses of Authentic Samples.—Authentic unsymmetrical disulphides were prepared by the reaction of thiols with sulphenyl chlorides in CCl$_4$[13] and purified by distillation: Ph–SS–R (b.p.): R = CH$_3$ (79—81° at 1 Torr) (lit.,[13a] 89—92° at 3 Torr); R = CH$_3$CH$_2$ (85—90° at 2 Torr); R = (CH$_3$)$_2$CH (90—92° at 2 Torr); R = CH$_3$- (CH$_2$)$_3$ (90—92° at 2 Torr) (lit.,[13b] 140—145° at 12 Torr); R = (CH$_3$)$_3$C (92—94° at 2 Torr); R = CH$_3$[CH$_2$]$_7$ (140° at 2 Torr); R = *p*-CH$_3$C$_6$H$_4$ (120—123° at 3 Torr). n- Butyl n-octyl disulphide had b.p. 85—86° at 2 Torr. Methyl benzenesulphinate was prepared from benzenesulphinyl chloride and methanol in CCl$_4$[14] and purified by column chromatography [silica gel, mesh 70—230; Merck; solvent hexane–propan-2-ol (20 : 1)], $\nu_{max.}$ 970, 990, and 1 130 cm⁻¹, δ(CDCl$_3$) 3.42 (3 H, s). Methyl benzenesulphonate was prepared from benzenesulphonyl chloride and sodium methoxide in methanol and purified by the same method,[15] $\nu_{max.}$ 997, 1 004, 1 180, 1 118, and 1 385 cm⁻¹, δ(CDCl$_3$) 3.72 (3 H, s).

Hexyl nitrite was prepared from hexan-1-ol and NaNO$_2$

[12] Z. Abel, *Phys. Chem.*, 1930, 148.
[13] (a) T. Aida, N. Furukawa, and S. Oae, *J.C.S. Perkin II*, 1976, 1432; (b) H. Britzinger and M. Langheck, *Chem. Ber.*, 1953, 86, 557; 1954, 87, 325.

[14] M. Kobayashi and N. Koga, *Bull. Chem. Soc. Japan*, 1966, 39, 1788.
[15] M. S. Mogan and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1948, 70, 375.

in the presence of H_2SO_4,[16] b.p. 46.5° at 32 Torr (lit.,[17] 64° at 76 Torr), $\nu_{max.}$ 1 605 and 1 655 cm^{-1}. N-Nitrosopiperidine was synthesized from piperidine hydrochloride on treatment with $NaNO_2$ and HCl,[18] b.p. 65—65.5° at 2 Torr (lit.,[19] 110° at 23 Torr). N-Phenylsulphonylpiperidine was obtained from piperidine and benzenesulphonyl chloride, m.p. 92—93° (lit.,[20] 92—93°).

Reaction of Phenyl Thionitrite with Hexan-1-ol.—A solution of N_2O_4 (2.0 mmol) in CCl_4 (1 ml) at ca. −20 °C was added to a solution of thiophenol (2.5 mmol) in ether (30 ml) with vigorous stirring in the dark. Immediately the solution became coloured. A solution of hexan-1-ol (4.8 mmol) in ether (20 ml) was slowly added at ca. −5 °C. After 2 h at ca. 5 °C, the solution was concentrated to ca. 5 ml under reduced pressure at 5—10 °C. The residue was diluted to 20 ml by $CHCl_3$ and was analysed by g.l.c. (Shimazu GC-6A column; SE-30; 2 m) showing Ph_2S_2 (70%), $CH_3[CH_2]_5ONO$ (18%), and recovered hexan-1-ol (64%).

Reaction of Phenyl Thionitrite with Excess of N_2O_4 and Methanol.—By treatment as above of phenyl thionitrite solution [from PhSH (2.0 mmol) and N_2O_4 (4.0 mmol)] with methanol (ca. 50 mmol), methyl benzenesulphinate (19%), methyl benzenesulphonate (11%), diphenyl disulphide (trace), and phenyl benzenethiolsulphonate (41%) were obtained. The yields and ratio of methyl sulphinate and sulphonate were determined by n.m.r. by comparison with authentic samples.

In order to observe the time dependence of product formation, addition of methanol to the thionitrite solution was carried out every 30 min at ca. −30 to −50 °C. Each reaction mixture was stirred at 0 °C for 5 min. After washing the mixture with 5% $NaHCO_3$, the ether layer was dried ($MgSO_4$) and evaporated. The products were separated by silica gel column chromatography [1 × 15 cm; solvent hexane–propan-2-ol (20 : 1)]. The results are shown in Figure 2.

Reaction of n-Butyl Thionitrite with Piperidine.—A solution of piperidine (12 mmol) in ether (20 ml) was added to n-butyl thionitrite (12 mmol) in ether (20 ml), washed with 5% $NaHCO_3$, and the mixture was left overnight at 25 °C in the dark. It was then washed with water (20 ml), the ether layer was dried ($MgSO_4$) and concentrated, and the products separated by column chromatography [2 × 20 cm; solvent hexane–propan-2-ol (20 : 1)] and analysed by g.l.c. showing n-butyl disulphide (19.5[4]) and N-nitrosopiperidine (8.5%).

Reaction of Thionitrites with Other Thiols.—The general

procedure for the reaction of the thionitrites with other thiols is as follows, taking phenyl t-butyl disulphide as an example. A solution of N_2O_4 (2.0 mmol) in CCl_4 (1 ml) at −20 °C was added to a solution of thiophenol (2.0 mmol) in ether (20 ml) with vigorous stirring in the dark. A solution of $(CH_3)_3CSH$ (2.0 mmol) in ether (10 ml) was added at ca. −5 °C. After 1 h at 0 °C, the mixture was washed with 5% $NaHCO_3$ solution and dried ($MgSO_4$). After removing ether, the crude product was purified by column chromatography [silica gel, 1 × 15 cm; solvent hexane–propan-2-ol (20 : 1)], yield 98%, b.p. 91—93° at 3 Torr (lit.,[13a] 89—92° at 3 Torr), $\delta(CCl_4)$ 1.29 (9 H, s).

All products were identified by comparing their retention times, b.p. or m.p., and i.r. and n.m.r. spectra with those of authentic samples. New compounds were also identified by elemental analysis: *phenyl t-butyl disulphide* (Found: C, 60.55; H, 6.95. $C_{10}H_{14}S_2$ requires C, 60.55; H, 7.1%); *isopropyl phenyl disulphide* (Found; C, 58.75; H, 6.4. $C_9H_{12}S_2$ requires Cl, 58.65; H, 6.55%); *n-octyl phenyl disulphide* (Found; C, 66.3; H, 8.15. $C_{14}H_{22}S_2$ requires C, 66.1; H, 8.7%); *n-butyl n-octyl disulphide* (Found; C, 61.45; H, 10.95. $C_{12}H_{26}S_2$ requires C, 61.45; H, 11.2%).

Reaction of Thionitrites with Sulphinic Acids.—The general procedure for the reaction of the thionitrites and sulphinic acids is as follows, taking phenyl toluene-*p*-thiolsulphonate as an example. A solution of phenyl thionitrite (2.0 mmol) was prepared from thiophenol (2.0 mmol) in ether (20 ml) and N_2O_4 (2.0 mmol) in CCl_4 (1 ml) at ca. −20 °C. A solution of toluene-*p*-sulphinic acid (2 mmol) in ether (20 ml) was added slowly to the thionitrite solution at ca. −5 °C with vigorous stirring in the dark. The colour disappeared after 20—30 min. After 2 h at 0 °C, the mixture was worked up as before. The crude product was purified by column chromatography [silica gel 1 × 15 cm; solvent hexane–propan-2-ol (20 : 1)], yield 80%, m.p. 75—76° (lit.,[21] 77—78°), $\nu_{max.}$ 1 145 and 1 335 cm^{-1}, $\delta(CCl_4)$ 2.42 (3 H, s).

By the same treatment, p-$CH_3C_6H_4$-$SSO_2C_6H_5$, p-Cl-C_6H_4-$SSO_2C_6H_5$, and $CH_3(CH_2)_3$-$SSO_2C_6H_4CH_3$-p were obtained: p-$CH_3C_6H_4$-$SSO_2C_6H_5$ (82%) had m.p. 50—51° (lit.,[21] 52—54°), $\nu_{max.}$ 1 150 and 1 330 cm^{-1}, $\delta(CCl_4)$ 2.37 (3 H, s); p-ClC_6H_4-$SSO_2C_6H_5$(73%) had m.p. 72—74° (lit.,[22] 72—73°), $\nu_{max.}$ 1 150 and 1 330 cm^{-1}, $CH_3(CH_2)_3$-$SSO_2C_6H_4CH_3$-p (61%) was a thin yellow liquid, $\nu_{max.}$ 1 145 and 1 330 cm^{-1}, $\delta(CCl_4)$ 2.40 (3 H, s) (Found: C, 54.05; H, 6.35. $C_{11}H_{16}S_2O_2$ requires C, 54.1; H, 6.55%).

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