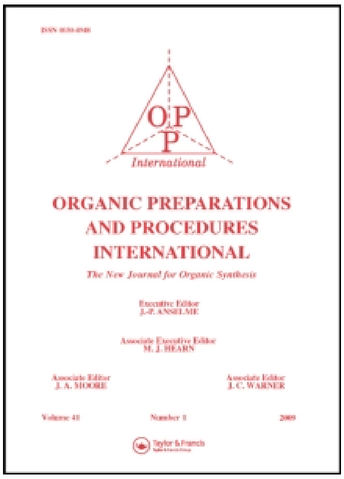

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ORGANIC THIONITRITES AND RELATED SUBSTANCES. A REVIEW

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INTRODUCTION

In the course of a systematic investigation on the oxidation of organic sulfur compounds, it was found that the oxidation of thiols, disulfides and sulfinic acids with N_2O_4 gives S-nitroso or S-nitro compounds such as thionitrites (I), thionitrates (II) or sulfonyl nitrites (III) as key intermediates.[1-3] Both thionitrites and thionitrates are less stable than corresponding oxygen analogs such as alkyl nitrites or alkyl nitrates. Hence, these S-nitroso and S-nitro compounds display very interesting chemical behavior which is merkedly different from those of the oxygen analogs. The sulfur-nitrogen bonds in S-nitroso and nitro compounds are weak compared with those of the corresponding oxygen-nitrogen bonds in nitrites (O-nitroso) and nitrates (O-nitro). Therefore, compounds containing S-NO bonds would be expected to be more reactive and be more useful in organic synthesis. Indeed, thionitrite (RSN=O) and thionitrate ($RSNO_2$) are not only good sulfenylating agents but are also powerful nitrosating agent; sulfonyl nitrites are even more powerful nitrosating agents. Aromatic amines are very readily converted to corresponding aryl derivatives upon treatment with S-nitroso or S-nitro compounds in the presence of cupric halides, halogen or disulfides. While

$R{-}S{-}NO$	$R{-}S{-}NO_2$	$R{-}SO_2{-}NO$
I	II	III

alkyl nitrates ($RONO_2$) are not diazotizing reagents, thionitrates ($RSNO_2$) are not only used as powerful diazotizing reagents but also display interesting chemical reactivity which would not be expected if thionitrates are regarded as simple analogs of alkyl nitrates. Since many of the reactions with S-nitroso and S-nitro compounds are so useful in organic synthesis, we now have summarized in this review the characteristic reactions and also synthetic applications of these S-nitroso and S-nitro compounds.

I. THIONITRITES

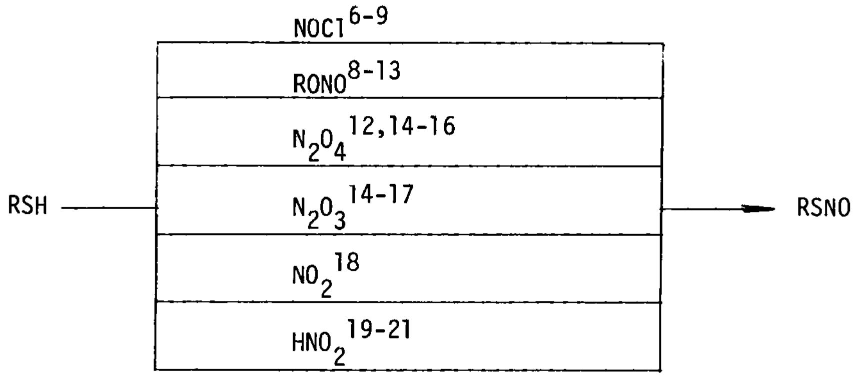
1. Syntheses of Thionitrites

As early as 1840, a red color was observed when thiols were treated with nitrous acid. Much later, Tasker and Jones reported that unstable red colored phenyl thionitrite <u>2</u> was formed when benzenethiol <u>1</u> was treated with nitrosyl chloride (Eq. 1).[4] However, <u>2</u> was found to decompose rapidly to give diphenyl disulfide <u>3</u> and nitrogen oxide.[4] The same authors also treated ethanethiol <u>4</u> with nitrosyl chloride to afford ethyl thionitrite <u>5</u> as a rather stable liquid (Eq. 2).[5]

$$\underset{\underline{1}}{PhSH} + NOCl \longrightarrow \underset{\underline{2}}{[\,PhSNO\,]} \longrightarrow \underset{\underline{3}}{(PhS\text{-})_2} + NO \qquad (1)$$

$$\underset{\underline{4}}{EtSH} + NOCl \longrightarrow \underset{\underline{5}}{EtSNO} \qquad (2)$$

Later, several thionitrites were prepared by treatment of thiols with nitrosyl chloride, alkyl nitrites, dinitrogen tetroxide, dinitrogen trioxide, nitrogen dioxide, nitrous acid and so on (Eq. 3). It was recently found that the treatment of thiols with N_2O_4 in inert solvents such as $CHCl_3$ or CCl_4 is the most convenient method for obtaining thionitrites.[2,15,16] Therefore, it would be quite interesting to see if free thiol groups in protein molecules can be masked to form -S-N=O groups by the same treatment.



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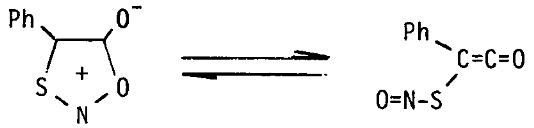
Meanwhile, Rao et al. studied the photolysis of dimethyl disulfide 6 in the vapor phase,[22] and considered the primary process to involve the direct formation of two $CH_3S\cdot$ radicals, each of which has an excess energy and is converted to methyl thionitrite 7 in the presence of nitrogen oxide (Eq. 4).

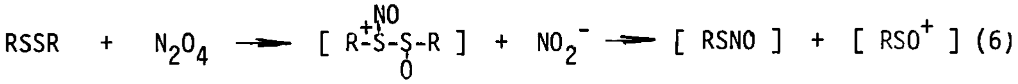
$$\underset{\underline{6}}{CH_3SSCH_3} \longrightarrow [\ CH_3S\cdot\ ] \xrightarrow{NO} \underset{\underline{7}}{CH_3SNO} \qquad (4)$$

A reversible formation of thionitrite 9 from 4-phenyl-1,3,2-oxathiazolylio-5-oxide 8 by photolysis was also reported (Eq. 5).[23,24]



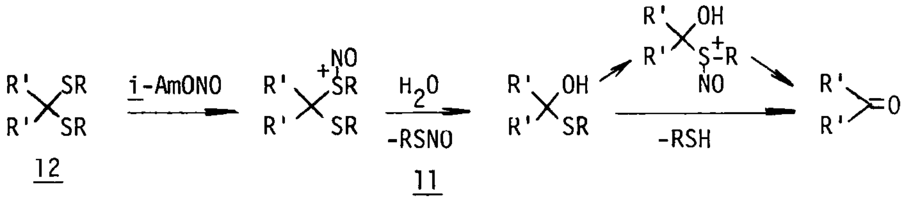
8 9 (5)

Formation of thionitrites 11 as the intermediate in the oxidation of disulfides 10 with N_2O_4 was first recognized by Oae et al. in 1978 (Eq. 6).[1]



$$\underset{\underline{10}}{RSSR} + N_2O_4 \longrightarrow [\ R\overset{+NO}{-S-}\underset{O}{S}-R\ ] + NO_2^- \longrightarrow \underset{\underline{11}}{[\ RSNO\ ]} + [\ RSO^+\ ] \qquad (6)$$

The presence of thionitrite 11 was also observed by Fuji *et al.* in the NMR spectrum of the red solution resulted in the reaction of dithioacetal 12 with isoamyl nitrite in $CDCl_3$ (Eq. 7).[25]



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Philippe *et al.* also reported that methyl thionitrite is found in the smoke of tobacco.[26]

2. Physical Properties of Thionitrites

Alkyl thionitrites are relatively stable and can be stored refrigerated in the dark. *t*-Butyl thionitrite is one of the most stable thionitrites and can be stored for several weeks. However, most aryl thionitrites are unstable and must be used *in situ*.

a) Color

Thionitrites are usually red or green colored compounds. For example, thionitrites 13 and 15 are deep green crystals.[6,21] Thionitrite 16 is a red gas[8] while thionitrite 14 is a red-green liquid.[12]

$(Ph)_3CSNO$	*t*-BuSNO	$ONSCMe_2CH(NHAc)CO_2H$	CF_3SNO
13	14	15	16

b) Dipole Moment

Thionitrites have nearly the same dipole moments (Table 1) as alkyl nitrites (2.3 D for EtONO).

c) Infrared Spectra

Infrared spectroscopic data have been reported,[2,8,12,13,27-29] and the

TABLE 1. Dipole Moments of Thionitrites[12]

Solvent	t-BuSNO	$(Ph)_3CSNO$	CH_3CN
CS_2	2.45	-	3.21
CCl_4	2.55	1.86	3.42
Benzene	2.63	1.93	3.47
Dioxane	2.71	-	3.56

frequencies of nitroso groups were compared with those of other nitroso compounds by Mason (Table 2).[8] Thionitrites show the IR absorption bands of N=O bond at longer wavelengths than those of corresponding alkyl nitrites. The same trend observed in the carbonyl stretching of ester and thioester, is explained in terms of the electronegativity difference between sulfur and oxygen.

TABLE 2. Streching and Bending Frequencis of the Nitroso Groups (cm^{-1})[8]

Compound	ν (NO)	δ (NO)
NOCl (s)	1946	245
(g)	1799	332
CF_3SNO (s)	1700	614, 610
EtSNO (l)	1536	620
t-BuSNO (l)	1490-1530	670, 662
MeONO (g) cis	1625	617
trans	1680	565
CF_3NO (g)	1595	405
t-BuNO	1574	

d) Ultraviolet and Visible Spectra

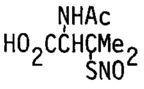
Ultraviolet and visible spectra are also known.[2,8,29,30] The absorptions at 250 nm (log $\varepsilon = 4.3$) and 360 nm (log $\varepsilon = 2.1$) were measured by Mason *et al*. on gaseous CF_3SNO.[8] Oae *et al*. also observed a strong absorption at 340 nm for liquid *t*-BuSNO,[2] which is responsible for the characteristic red color of this thionitrite.

e) ^{15}N-NMR Spectroscopic Data

^{15}N-NMR chemical shifts data of triphenylmethyl thionitrite ($Ph_3CS^{15}NO$) was reported by Bonnett *et al*.[31] The nitrogen atom (^{15}N) in this thionitrite shows δ 785.2 ppm in $CDCl_3$ (0.5 M) relative to $^{15}NH_4^+$ as nitrate (5 M-$^{15}NH_4NO_3$ in 2 M-HNO_3).

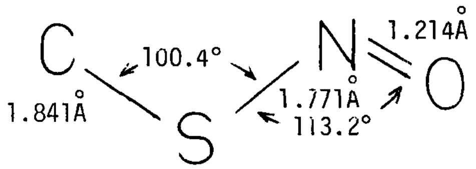
f) X-Ray Analysis and Molecular Structure

The stable thionitrite 15 was prepared by Field *et al*. and the molecular structure of this compound was determined by X-ray.[21] The C-S bond (1.841 Å) is rather long and the S-N bond (1.771 Å) is nearly the same as the calculated bond length with Pauling's covalent bond radii.



$HO_2C\overset{NHAc}{CH}\underset{SNO}{CMe_2}$

15



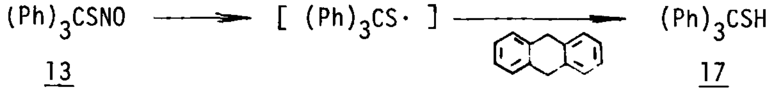
3. Reactions of Thionitrites

a) Thermal Decomposition

Almost all the thionitrites are unstable at room temperature and decompose to give corresponding disulfides and nitrogen oxide. Ethyl thionitrite 5 undergo about 2% decomposition at 13° after 4.5 hrs and is completely decomposed at 70-130° after 2 hrs.[10] However, tertiary thionitrites such as 13, 14, and 15 are stable at room temperature, but decompose upon heating to afford corresponding disulfides.[7,21,32]

$EtSNO^{10}$	$(Ph)_3CSNO^{7,21}$	$\underline{t}$-$BuSNO^{32}$	$ONSCMe_2CH(NHAc)CO_2H^{21}$
5	13	14	15

Thionitrite 13 was shown to decompose thermally to give triphenylmethanethiol 17 in the presence of a radical scavenger such as 9,10-dihydroanthracene (Eq. 8).[33]

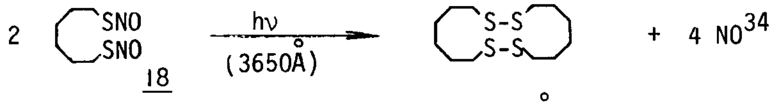


(8)

b) Photolysis

Thionitrites 11 and 18 were also shown to decompose upon photolysis to give corresponding disulfides and nitrogen oxide (Eq. 9,10).[34,35] Barrett

$$2\,\underset{\underline{11}}{\mathrm{RSNO}} + h\nu\ (3650\text{Å}) \longrightarrow \mathrm{RSSR} + 2\,\mathrm{NO}^{34,35} \qquad (9)$$



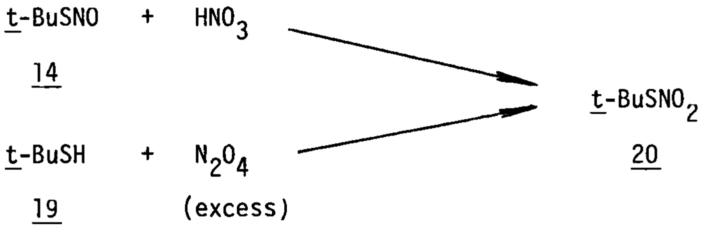
(10)

et al. considered that the absorption af 3650Å-radiation resulted in excitation to the extent of 79 Kcal/mol, which is sufficient to cause the fission of the bond.[35] The process can be formulated as follows (Eq. 11).[35]

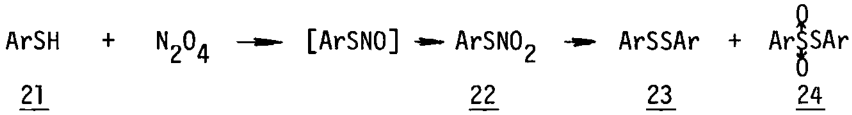
$$\begin{gathered} \mathrm{PhCH_2SNO} \xrightarrow{h\nu} \mathrm{PhCH_2SNO^*} \longrightarrow \mathrm{PhCH_2\cdot} + \mathrm{NO\cdot} \\ \mathrm{PhCH_2\cdot} + \mathrm{PhCH_2SNO} \longrightarrow \mathrm{PhCH_2SSCH_2Ph} \end{gathered} \qquad (11)$$

c) Oxidation

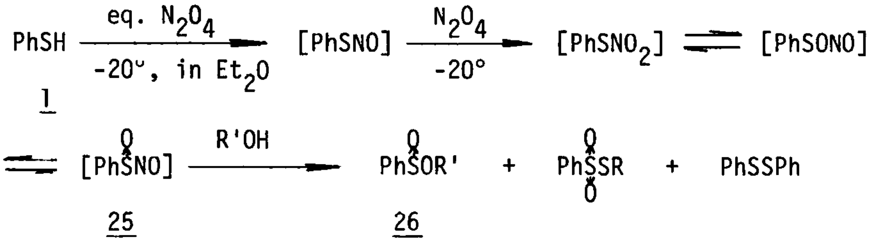
Thionitrite 14 was shown to be oxidized further with fuming nitric acid in a vigorous reaction, to give t-butyl thionitrate 20.[36] Oae et al. found that thionitrate 20 can be prepared nearly quantitatively by treatment of thiol 19 with an excess N_2O_4 (Eq. 12).[2,37] Oxidation of aryl thiols 21 with excess N_2O_4 at -60° also gives aryl thionitrates 22 in good yields. However, these compounds are unstable at room temperature and decompose to give corresponding disulfides 23 and thiolsulfonates 24 (Eq. 13).[2] When the reaction mixture of thiol 1 with N_2O_4 was quenched with MeOH or i-PrOH, alkyl benzenesulfinate 26 was obtained, suggesting that perhaps benzenesulfinyl nitrite 25 is the reaction intermediate (Eq. 14).[2,37]



$$\underset{14}{t\text{-}BuSNO} + HNO_3 \rightarrow \underset{20}{t\text{-}BuSNO_2} \leftarrow \underset{19}{t\text{-}BuSH} + \underset{(excess)}{N_2O_4} \quad (12)$$



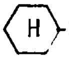
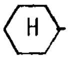
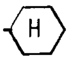
$$\underset{21}{ArSH} + N_2O_4 \rightarrow [ArSNO] \rightarrow \underset{22}{ArSNO_2} \rightarrow \underset{23}{ArSSAr} + \underset{24}{Ar\overset{O}{\underset{O}{S}}SAr} \quad (13)$$



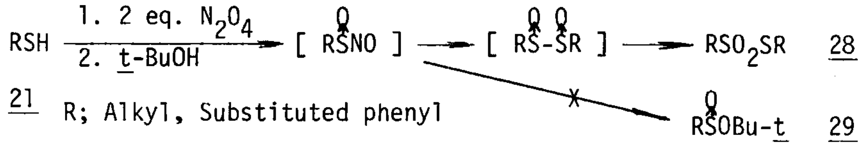
$$\underset{1}{PhSH} \xrightarrow[-20^\circ,\ in\ Et_2O]{eq.\ N_2O_4} [PhSNO] \xrightarrow[-20^\circ]{N_2O_4} [PhSNO_2] \rightleftharpoons [PhSONO] \rightleftharpoons \underset{25}{[Ph\overset{O}{S}NO]} \xrightarrow{R'OH} \underset{26}{Ph\overset{O}{S}OR'} + Ph\overset{O}{\underset{O}{S}}SR + PhSSPh \quad (14)$$

Oae et al. have also shown that when thiols 21 are mixed with excess N_2O_4 at -20-0° and then quenched with t-BuOH, the corresponding thiolsulfonates 28 can be obtained in good yields as shown in Table 3. Sulfinate 29 was not obtained because of the steric hindrance of t-butyl group.[2,37] Thus, symmetrical thiolsulfonates 28 can be prepared by this simple one-step procedure (Eq. 15). Although, thiolsulfonate 27 cannot be prepared by this direct oxidation of thiol 19 with N_2O_4 and subsequent treatment with t-BuOH, it can be prepared by the treatment of thionitrate 20 with pyridine (Eq. 16).[2]

TABLE 3. Reactions of Thiols with N_2O_4[2,37,38]

Thiol	Reaction Time(min)	Reaction Temp(°C)	$\frac{N_2O_4}{RSH}$[a)]	Product	Isolated yield(%)
PhSH	5	ca. -15	2	$PhSSO_2Ph$	81
-SH	5	ca. -15	2	$-SSO_2-$	62
n-$C_6H_{13}SH$	5	ca. -10	2	n-C_6H_{13}-$SSO_2C_6H_{13}$-n	63
t-BuSH	ca. 15	ca. 25	2.5	t-$BuSNO_2$	ca. 80-100

a) Mol ratio.



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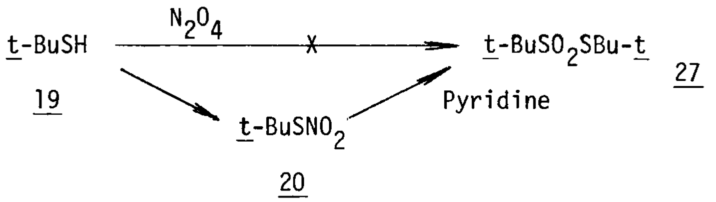
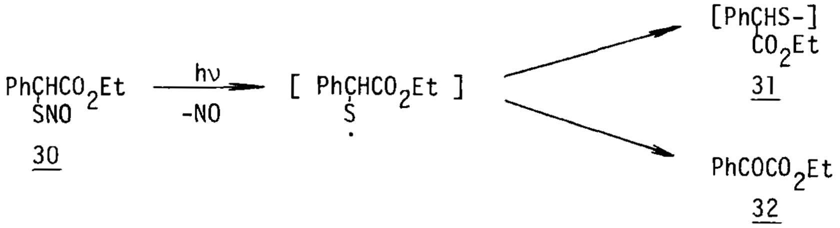


(16)

Earlier, Lecher et al. passed air into thionitrite 5 for about 3 hrs and obtained corresponding diethyl disulfide and N_2O_4 (Eq. 17).[9] However, they could not isolate any of the primary product of the auto-oxidation.

$$\underset{\underline{5}}{2\ \mathrm{EtSNO}} + O_2 \longrightarrow (\mathrm{EtS-})_2 + N_2O_4 \qquad (17)$$

Holm et al. obtained a small amount of ethyl phenylglyoxylate 32 (2%) upon photolysis of ethyl (nitrosothio)-phenylglyoxylate 30 in the presence of oxygen. The main product was corresponding disulfide 31 (Eq. 18).[23]



(18)

d) Reduction

Thionitrite 33 can be reduced by Hg(II) ion to give thiol 34 (Eq. 19).[20] This reaction was used for analysis of mercapto group by Saville.[20]

$$\underset{33}{\text{Cysteine-SNO}} \xrightarrow{Hg^{2+}} \underset{34}{\text{Cysteine-SH}} + HNO_2 \qquad (19)$$

Field et al. obtained disulfide 35 upon reduction of thionitrite 15 with $NaBH_4$ (Eq. 20).[21]

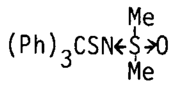
$$\underset{15}{ONSCMe_2CH(NHAc)CO_2H} \xrightarrow[\text{EtOH}\ \ 56\%]{NaBH_4\ \text{in}} \underset{35}{[-SCMe_2CH(NHAc)CO_2H]_2} \qquad (20)$$

e) Reaction with Triphenylphosphine

Haake et al. isolated phosphinimine 37 as orange colored crystals upon treatment of thionitrite 13 with 2 eq. of triphenylphosphine 36 (Eq. 21).[39]

$$\underset{13}{(Ph)_3CSNO} + \underset{36}{(Ph)_3P} \xrightarrow[25°,\ \text{ca. } 100\%]{\text{in benzene}} \underset{37}{(Ph)_3CSN{=}P(Ph)_3} \qquad (21)$$

When this reaction was carried out in the presence of dimethyl sulfoxide, N-triphenylmethylthio-dimethylsulfoximide 38 was obtained in addition to the phosphineimine 37 (Eq. 22).[39]



$$\underline{13} + \underline{36} + \text{DMSO} \longrightarrow \underset{(30\%)}{\underline{37}} + \underset{\underline{38}\ (11\%)}{(\text{Ph})_3\text{CSN}\leftarrow\overset{\text{Me}}{\underset{\text{Me}}{\text{S}}}\rightarrow\text{O}} \qquad (22)$$

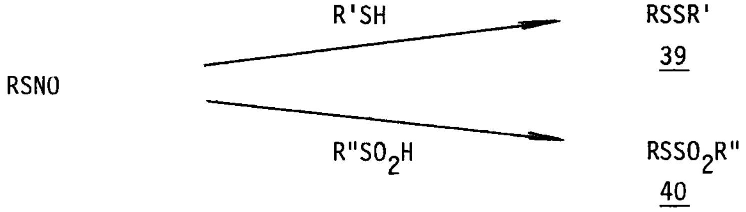
f) Reactions with Thiols or Sulfinic Acids

The reaction of thionitrite (RSNO) with thiols or sulfinic acids give unsymmetrical disulfides 39 and thiolsulfonates 40 in good yields.[15,16] A few typical results are listed in Table 4. This is probably one of the most convenient procedures to prepare unsymmetrical disulfides 39 and thiolsulfonates 40, since the preparation can be carried out in a one-pot process. In a typical run, to an ethereal solution of a thiol is added either a chloroform or a carbon tetrachloride solution of an equimolar amount of N_2O_4. Immediately either greenish or reddish color appears. Then an equimolar amount of either another thiol or sulfinic acid is added into the reaction mixture. When the typical color of thionitrite disappears, neutralization with weak alkaline solution and subsequent evaporation of the solvent give the desired unsymmetrical disulfide or thiolsulfonate in an excellent yield (Eq. 23).

TABLE 4. Reactions of Thionitrites with Thiols or Sulfinic Acids[15,16]

RSNO	RSH or RSO_2H	Product	Yield (%)
PhSNO	t-BuSH	PhSSBu-t	$98^{b)}$
PhSNO	p-TolSH	PhSSTol-p	$81^{a)}$
n-C_8H_{17}SNO	n-BuSH	n-C_8H_{17}SSBu-n	$81^{a)}$
PhSNO	p-TolSO_2H	PhSSO_2Tol-p	$74^{b)}$

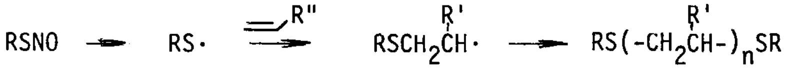
a) GC yield. b) Isolated yield.



(23)

g) Reaction with Olefins

Lecher *et al*. reported that thionitrites did not lose their colors upon treatment with olefins at 25°.[10] However, Field *et al*. obtained hard polymers from a mixture of thionitrite 15 and such olefins as methyl methacrylate in the presence of benzoyl peroxide; they also obtained polymers by UV irradiation of olefins and thionitrite 15 (Eq. 24).[21]



$$RSNO \longrightarrow RS\cdot \xrightarrow{=\!/R''} RSCH_2\overset{R'}{C}H\cdot \longrightarrow RS(-CH_2\overset{R'}{C}H-)_nSR \qquad (24)$$

15 R; $-CMe_2CH(NHAc)CO_2H$

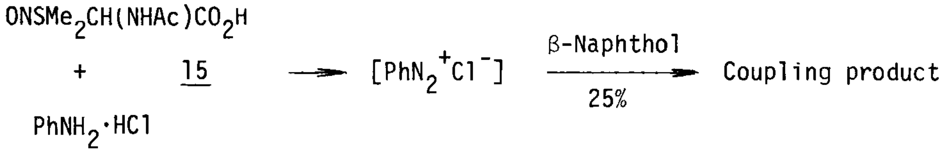
h) Reaction with Amines

Treatment of thionitrites with cyclic secondary amines afforded N-nitrosamines (Eq. 25).[16] N-Methylaniline was also converted to N-nitroso-N-methylaniline with thionitrite 14 in a good yield (Eq. 26).[38]

$$RSNO + R'_2NH \longrightarrow R'_2NNO + RSSR \qquad (25)$$

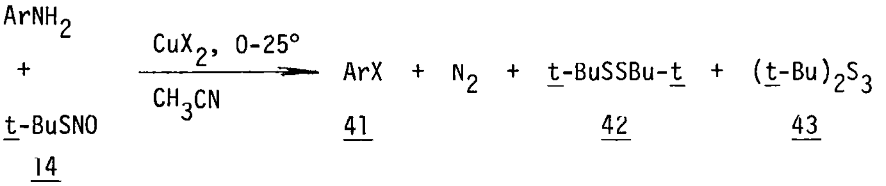
$$PhNHMe + \underset{\underline{14}\ 1.7\ eq.}{\underline{t}\text{-}BuSNO} \xrightarrow[3\ days,\ 92\%]{in\ Et_2O,\ 25°} PhNMeNO \qquad (26)$$

Field *et al*. suggested the incipient formation of benzenediazonium chloride in the reaction of thionitrite 15 with aniline hydrochloride, in view of the formation of a coupling product upon treatment with β-naphthol (Eq. 27).[21]



$$\begin{array}{c} ONSMe_2CH(NHAc)CO_2H \\ + \quad \underline{15} \\ PhNH_2\cdot HCl \end{array} \longrightarrow [PhN_2^+Cl^-] \xrightarrow[25\%]{\beta\text{-Naphthol}} \text{Coupling product} \quad (27)$$

It was independently found in our laboratories that various arylamines react readily with thionitrite 14 in the presence of anhydrous copper(II) halides to afford the corresponding halides 41 in excellent yields (Eq. 28).[40,41] This reaction proceeds below room temperature, while the similar reaction with alkyl nitrite[43,44] requires heating in many cases. The results are summarized in Table 5.



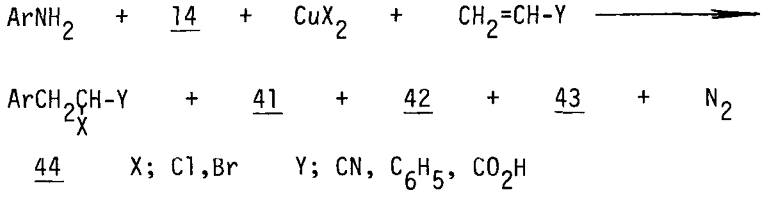
$$\begin{array}{c} ArNH_2 \\ + \\ \underline{t}\text{-BuSNO} \\ \underline{14} \end{array} \xrightarrow[CH_3CN]{CuX_2,\ 0\text{-}25°} \underset{\underline{41}}{ArX} + N_2 + \underset{\underline{42}}{\underline{t}\text{-BuSSBu-}\underline{t}} + \underset{\underline{43}}{(\underline{t}\text{-Bu})_2S_3} \quad (28)$$

TABLE 5. Deamination of Arylamines with t-BuSNO and Anhydrous Copper(II) Halides[40,41]

$ArNH_2$	Yield (%)	
	ArCl	ArBr
$\underline{p}\text{-}NO_2C_6H_4NH_2$	98[a)]	78[a)]
$\underline{p}\text{-}ClC_6H_4NH_2$	78[b)]	71[b)]
$C_6H_5NH_2$	86[b)]	58[b)]
$\underline{p}\text{-}MeOC_6H_4NH_2$	61[b)]	36[b)]
$\underline{p}\text{-}HOC_6H_4NH_2$	57[a)]	40[a)]

a) Isolated yield. b) GC yield.

When this reaction is carried out in the presence of several olefins, the Meerwein reaction takes place and the corresponding 2-aryl-1-haloethanes 44 are obtained as the main products (Eq. 29).[41] The results are listed in Table 6.



$$\mathrm{ArNH_2} + \underline{14} + \mathrm{CuX_2} + \mathrm{CH_2{=}CH{-}Y} \longrightarrow \mathrm{ArCH_2\underset{X}{C}H{-}Y} + \underline{41} + \underline{42} + \underline{43} + \mathrm{N_2} \qquad (29)$$

44 X; Cl,Br Y; CN, C_6H_5, CO_2H

TABLE 6. Deamination of Arylamines with t-BuSNO and Anhydrous Copper(II) Halides in the Presence of Acrylonitrile[41]

$ArNH_2$	Product and yield (%)	
	$ArCH_2\underset{X}{C}HR$	ArX
p-$NO_2C_6H_4NH_2$	$48^{a)}$ $(32^{b)})$	$32^{a)}$
o-$NO_2C_6H_4NH_2$	$29^{a)}$ $(21^{b)})$	$25^{a)}$
$C_6H_5NH_2$	$48^{a)}$ $(31^{b)})$	$34^{a)}$
p-$MeOC_6H_4NH_2$	$50^{a)}$ $(40^{b)})$	$43^{a)}$

a) GC yield. b) Isolated yield.

The reaction of disulfide 42 with $CuCl_2$ under similar conditions affords both the trisulfide 43 and tetrasulfide 45 (Eq. 30). Probably in the presence of thionitrite 14, the anionic intermediate t-$BuSS^-$ or radical intermediate t-BuSS· reacts with the thionitrite 14 to give the trisulfide 43 (Eq. 31).[44]

$$\underset{\underline{42}}{(t\text{-}Bu)_2S_2} + CuCl_2 \longrightarrow \underset{\underline{43}}{(t\text{-}Bu)_2S_3} + \underset{\underline{45}}{(t\text{-}Bu)_2S_4} \qquad (30)$$

$$\begin{array}{ccccccc} t\text{-BuSNO} & + & CuCl_2 & \longrightarrow & (t\text{-Bu})_2S_2 & + & (t\text{-Bu})_2S_3 \\ \underline{14} & & & & \underline{42} & & \underline{43} \end{array} \qquad (31)$$

II. THIONITRATES

1. Syntheses of Thionitrates

As described previously in the oxidation of thionitrites [I-3, c)], thionitrate 20 had been prepared by further oxidation of thionitrite 14 with fuming nitric acid[36] or N_2O_4 (Eq. 32).[12] It was found that stable t-alkyl thionitrates 47 can be prepared in good yields by treating thiols 46 with excess N_2O_4 (Eq. 33).[2,37] The aryl thionitrates 22 were also isolated in good yields as unstable white crystals upon treatment of the corresponding aryl thiols 21 with excess N_2O_4 in hexane at low temperatures (ca. -60°) (Eq. 34).[2] Many of these thionitrates 22 decomposed readily at room temperature and some aryl thionitrates 22 are stable at low temperatures; generally other thionitrates are not stable enough to be isolated in pure form.[2]

$$\begin{array}{ccccc} t\text{-BuSNO} & + & HNO_3 \text{ or } N_2O_4 & \longrightarrow & t\text{-BuSNO}_2 \\ \underline{14} & & & & \underline{20} \end{array} \qquad (32)$$

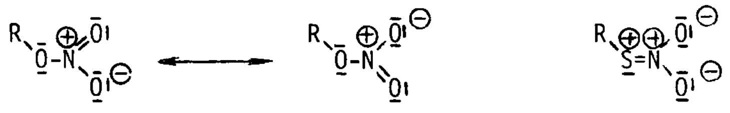
$$\begin{array}{ccccc} RSH & \xrightarrow[2 \text{ eq. } N_2O_4]{20\text{-}30°} & [\ RSNO\ ] & \longrightarrow & RSNO_2 \\ \underline{46} & R;\ t\text{-alkyl} & & & \underline{47} \end{array} \qquad (33)$$

$$\begin{array}{ccccc} ArSH & \xrightarrow[1.5\text{-}2 \text{ eq. } N_2O_4]{-60°} & [\ ArSNO\ ] & \longrightarrow & ArSNO_2 \\ \underline{21} & & & & \underline{22} \end{array} \qquad (34)$$

Ar; p-Tol, p-ClC_6H_5, p-BrC_6H_5

2. Physical Properties of Thionitrates

Isolated thionitrates are colorless liquids or white crystals.[2] Kresze et al. reported that dipole moment of t-$BuSNO_2$ is larger (3.73 D) than those of alkyl nitrates (e.g., $EtONO_2$ 2.9 D) and other nitro compounds (e.g., t-$BuNO_2$ 3.5 D).[12] This may due to the relatively lower electronegativity of sulfur atom than that of oxygen atom.[12]

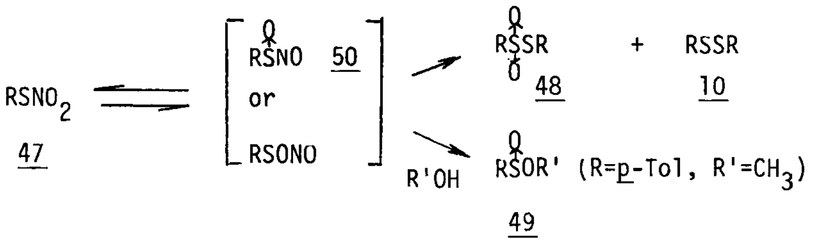


t-$BuSNO_2$ displays an infrared absorption band which is at a longer wavelength (1510 cm^{-1}) than that of corresponding alkyl nitrite (t-$BuONO_2$; 1608 cm^{-1}) due to the electronegativity difference between sulfur and oxygen.[2]

3. Reactions of Thionitrates

a) Thermal Decomposition

Thionitrates 47 (R=Aryl) decompose at room temperature to afford corresponding thiolsulfonates 48 and disulfides 10. Stable thionitrate 47 (R=t-Bu) also undergo thermolysis at above 100° to give corresponding thiolsulfonate 48 and disulfide 10 (Eq. 35).[2] Sulfinyl nitrites 50 are believed to be the intermediates, because when thionitrate 47 (R=p-Tol) was quenched with excess methanol, methyl p-toluenesulfinate 49 was obtained in 17% yield (Eq. 36).[2]



$$\underset{\mathbf{47}}{RSNO_2} \rightleftharpoons \left[\begin{array}{l} RS(O)NO \quad \mathbf{50} \\ \text{or} \\ RSONO \end{array}\right] \rightarrow \underset{\mathbf{48}}{RS(O)_2SR} + \underset{\mathbf{10}}{RSSR} \qquad (35)$$

$$\left[\ \right] \xrightarrow{R'OH} \underset{\mathbf{49}}{RS(O)OR'} \ (R=p\text{-Tol},\ R'=CH_3) \qquad (36)$$

b) Reaction with Amines

The most interesting aspect of thionitrates ($RSNO_2$) is that they can be used as very effective diazotizing agents in neutral aprotic media while corresponding alkyl nitrates ($RONO_2$) do not react readily with amines and hence cannot be used as diazotizing agents. Oae et al. found that reactions of various arylamines with thionitrate 20 in the presence of anhydrous copper(II) halides under mild conditions give corresponding aryl halides 41 in excellent yields (Eq. 37), (Table 7).[40,41]

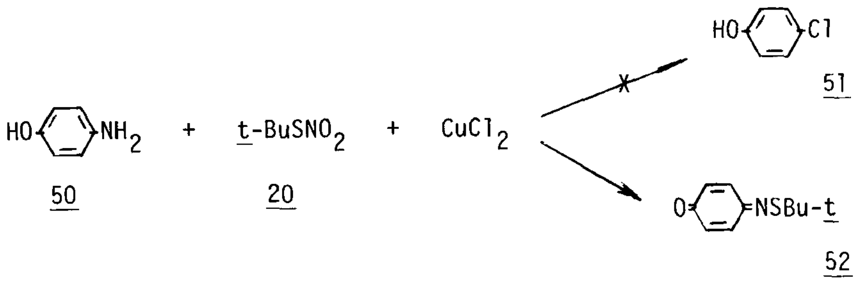
$$\mathrm{ArNH_2} + \underset{\underline{20}}{\underline{\mathrm{t}}\text{-}\mathrm{BuSNO_2}} + \mathrm{CuX_2} \xrightarrow[25^\circ,\ 2\ \mathrm{hrs}]{\mathrm{CH_3CN}} \underset{\underline{41}}{\mathrm{ArX}} + \underset{\underline{42}}{(\underline{\mathrm{t}}\text{-}\mathrm{Bu})_2\mathrm{S}_2} + \underset{\underline{43}}{(\underline{\mathrm{t}}\text{-}\mathrm{Bu})_2\mathrm{S}_3} + \mathrm{N_2} \quad (\mathrm{X = Cl, Br}) \tag{37}$$

TABLE 7. Deamination of Arylamines with t-$BuSNO_2$ and Anhydrous Copper(II) Halides at Room Temperature[40,41]

$ArNH_2$	Yield (%)	
	ArCl	ArBr
p-$NO_2C_6H_4NH_2$	98[a)]	74[a)]
p-$HO_2CC_6H_4NH_2$	86[a)]	75[a)]
p-$ClC_6H_4NH_2$	71[b)]	55[b)]
$C_6H_5NH_2$	82[b)]	83[b)]
p-$MeOC_6H_4NH_2$	63[b)]	57[b)]

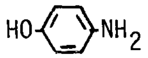
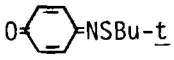
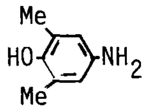
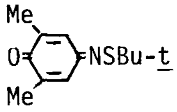
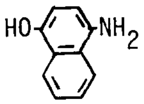
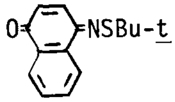
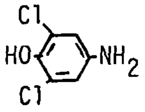
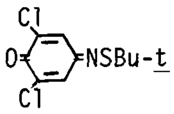
a) Isolated yield. b) GC yield.

The reaction of p-hydroxyaniline 50 with the thionitrate 20 in the presence of CuX_2 is different. The reaction does not give the corresponding halide 51, but affords N-(t-butylthio)-p-benzoquinone monoimine 52 in 40% yield (Eq. 38).[40,41] Various p-hydroxyaniline derivatives were found to be converted easily to corresponding N-(t-alkylthio)-p-benzoquinone monoimines with thionitrates even without CuX_2.[2,45] All these imines have vivid yellow colors due to the strong absorption ($\varepsilon_{max} > 10^4$) near 400 nm. Although N-alkylthio-p-benzoquinone monoimines can be prepared from N-halo p-benzoquinone monoimines,[46,47] the use of thionitrates constitutes a new



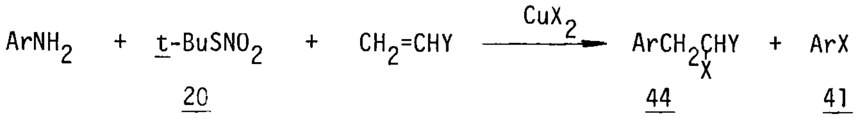
(38)

TABLE 8. Reactions of t-$BuSNO_2$ with p-Aminophenols[2,45]

p-Aminophenol	Product	Isolated yield (%)
		40
		47
		15
		45

one-step synthetic method from p-aminophenols (Table 8).

As mentioned previously (Eq. 29), 2-aryl-1-haloethanes 44 were readily obtained (Meerwein arylation) when various arylamines were treated with thionitrate 20 and anhydrous copper(II) halides in the presence of olefins (Eq. 39), (Table 9).[41]



$$\underset{20}{ArNH_2 + t\text{-}BuSNO_2} + CH_2{=}CHY \xrightarrow{CuX_2} \underset{44}{ArCH_2\underset{X}{C}HY} + \underset{41}{ArX} \qquad (39)$$

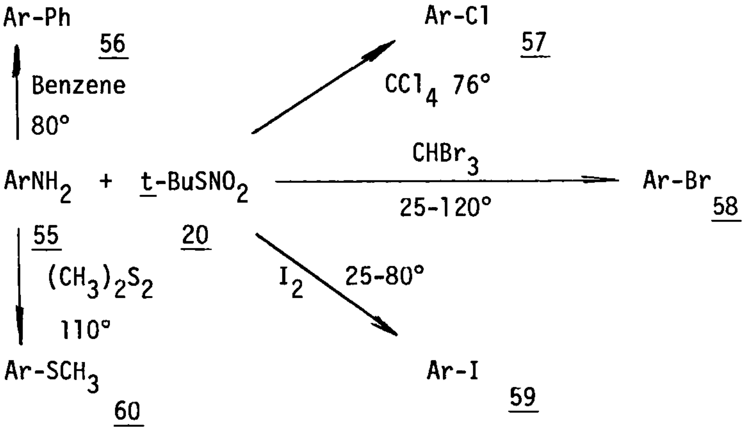
TABLE 9. Deamination with t-BuSNO$_2$ and Anhydrous Copper(II) Halides in the Presence of Olefins at Room Temperature[41]

ArNH$_2$	(CuX$_2$)	(CH$_2$=CHY)	Product and yield (%)	
	X	Y	$ArCH_2\underset{X}{C}HR$	ArX
p-NO$_2$C$_6$H$_4$NH$_2$	Cl	CN	78$^{a)}$(65$^{b)}$)	11$^{a)}$
p-NO$_2$C$_6$H$_4$NH$_2$	Cl	Ph	62$^{a)}$(58$^{b)}$)	20$^{a)}$
p-NO$_2$C$_6$H$_4$NH$_2$	Cl	CO$_2$Et	49$^{a)}$(35$^{b)}$)	33$^{a)}$
C$_6$H$_5$NH$_2$	Cl	c)	40$^{a)}$(31$^{b)}$)	20$^{a)}$
C$_6$H$_5$NH$_2$	Br	CO$_2$H	41$^{a)}$(38$^{b)}$)	33$^{a)}$
C$_6$H$_5$NH$_2$	Cl	CO$_2$Et	56$^{a)}$(36$^{b)}$)	22$^{a)}$

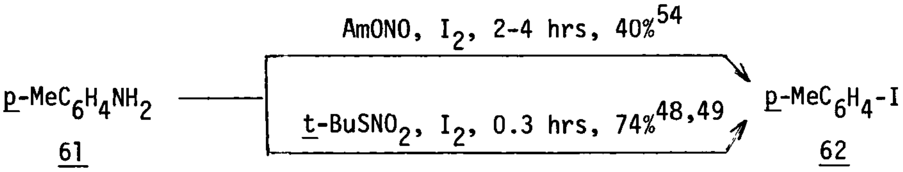
a) GC yield. b) Isolated yield. c) Methyl methacrylate was used.

The oxygen analogs, e.g., i-amyl nitrate 54 do not isomerize to the corresponding O-nitroso derivative, hence does not react with 4-chloroaniline 53 in benzene. One fascinating aspect is that various arylamines 55 react readily in the absence of any redox metal ion with thionitrate 20 with carbon tetrachloride, bromoform, iodine, benzene and dimethyl disulfide, affording deaminated products such as aryl halides 57-59, biphenyls 56 and aryl methyl sulfides 60 in good yields.[48,49] The results are illus-

$$\underset{53}{p\text{-}ClC_6H_4NH_2} + \underset{54}{i\text{-}AmONO_2} \xrightarrow[\times]{\text{in benzene}} p\text{-}ClC_6H_4\text{-}Ph$$



(40)



(41)

$$\underset{63}{PhNH_2} + AmONO + I_2 \longrightarrow \underset{64}{Ph\text{-}I} + \underset{65}{I\text{-}C_6H_4\text{-}I} + \underset{66}{Ph_2}{}^{54} \qquad (42)$$

TABLE 10. A Few Representative Reactions of Arylamines with t-BuSNO$_2$ in Various Solvents[48,49]

$ArNH_2$	Solvent	Product	Yield(%)
p-$NO_2C_6H_4NH_2$	Benzene	p-$NO_2C_6H_4$-Ph	75[a)]
p-$BrC_6H_4NH_2$	Benzene	p-BrC_6H_4-Ph	76[a)]
p-$BrC_6H_4NH_2$	Me_2S_2	p-BrC_6H_4-SMe	88[b)]
p-$NO_2C_6H_4NH_2$	$CHBr_3$	p-$NO_2C_6H_4$-Br	80[a)]
p-$ClC_6H_4NH_2$	CCl_4	p-ClC_6H_4-Cl	46[a)]
p-$MeC_6H_4NH_2$	Benzene/I_2	p-MeC_6H_4-I	79[a)]

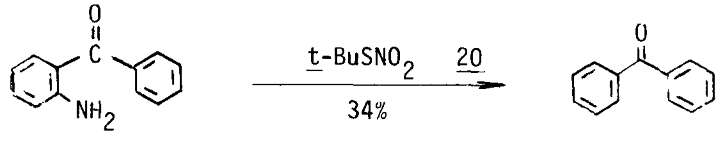
a) GC yield. b) Isolated yield.

trated in equation (40) and listed in Table 10. Among these reactions, the reaction of arylamines with dimethyl disulfide was found to be extremely useful, since the reaction can be carried out with very little formation of bad smelling sulfur compounds. Other disulfides can also be used to replace amino group with RS moiety.

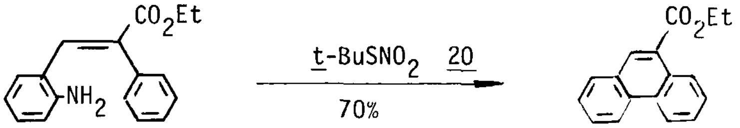
Alkyl nitrites (RONO) may also be used in similar reactions.[50-54] However, chlorination or bromination generally require much longer reaction times (2 hrs at 100°[53]) than those of thionitrate 20 (5-60 min. at 25-120°[48,49]). *p*-Toluidine 61 can be converted to *p*-iodotoluene 62 with amyl nitrite in the presence of iodine after a long reaction time in a lower yield (Eq. 41).[54] Iodobenzene 64 can also be obtained from aniline 63 upon treatment with amyl nitrite and iodine, however the yield is rather low due to the formation of by-products 65 and 66 (Eq. 42). In the reaction in benzene, the reaction time and the yields of biphenyls 56 are nearly the same as those with alkyl nitrites.[50-52] Formation of nitrogen gas was established by MS spectroscopy, thus establishing that the reaction to proceed *via* the diazonium salts that decompose to aryl radicals which then react with the solvent to afford the corresponding deaminative substitution products.[48,49] Incidentally, thionitrites (RSNO) may not be used for these uncatalyzed deaminative reactions owing to their thermal instability.[48] The following mechanism has been postulated. *t*-BuSOH is a good reducing agent and hence is considered to act as an excellent redox system to generate aryl radicals (Eq. 43).

$$\begin{array}{l} \underset{\underline{20}}{\underline{t}\text{-BuSNO}_2} \rightleftharpoons \underline{t}\text{-BuSONO} \xrightarrow{\text{ArNH}_2} \underline{t}\text{-BuSO}^- + \text{Ar}\overset{+}{\text{N}}\text{H}_2\text{NO} \longrightarrow \\ \\ \underline{t}\text{-BuSOH} + \text{ArN}_2^+\,\text{OH}^- \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{H}_2\text{O} + \underline{t}\text{-BuSO}_2\text{Bu-}\underline{t} \end{array} \qquad (43)$$

Thionitrate 20 can also be used for the Pschorr type reactions. Aryl amines 67 and 69 afford corresponding ring-closed products 68 and 70 (Eqs. 44 and 45).[38]

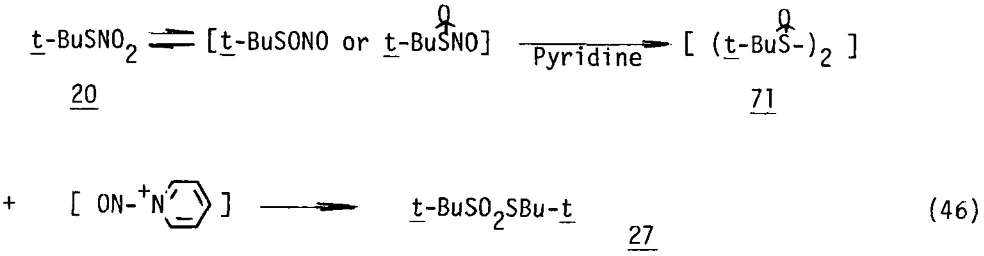


67 68 (44)



69 70 (45)

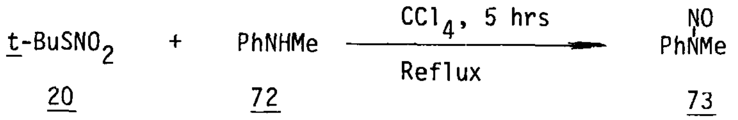
On the other hand, thionitrate 20 was decomposed with pyridine to give thiolsulfonate 27 quantitatively. This reaction is considered to proceed via incipient formation of α-disulfoxide 71 (Eq. 46).[2]



$$\underset{20}{t\text{-BuSNO}_2} \rightleftharpoons [t\text{-BuSONO or } t\text{-Bu}\overset{O}{S}\text{NO}] \xrightarrow[\text{Pyridine}]{} \underset{71}{[\,(t\text{-Bu}\overset{O}{S}\text{-})_2\,]}$$

$$+ \quad [\,\text{ON-}^{+}\text{N}\,] \longrightarrow \underset{27}{t\text{-BuSO}_2\text{SBu-}t} \qquad (46)$$

Thionitrate 20 was also found to react with secondary amine 72 to give N-nitrosamine 73 in 53% yield (Eq. 47).[38]

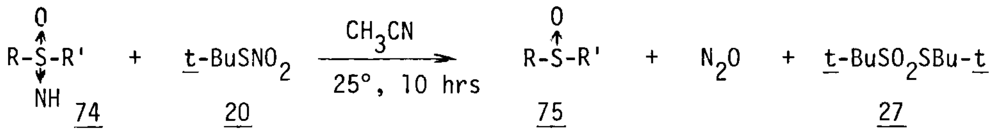


$$\underset{20}{t\text{-BuSNO}_2} + \underset{72}{\text{PhNHMe}} \xrightarrow[\text{Reflux}]{\text{CCl}_4\text{, 5 hrs}} \underset{73}{\text{Ph}\overset{\text{NO}}{\text{N}}\text{Me}} \qquad (47)$$

c) Reaction with Sulfoximides

Oae et al. have recently shown that deimination of diaryl sulfoximides

74 proceeds readily with thionitrate 20 affording the corresponding sulfoxides 75 (Eq. 48).[55] The gas evolved in this reaction is nitrous oxide and not nitrogen. The results are listed in Table 11.



$$\underset{\underset{74}{NH}}{\overset{O}{R-S-R'}} + \underset{20}{t\text{-}BuSNO_2} \xrightarrow[25°,\ 10\ hrs]{CH_3CN} \underset{75}{\overset{O}{R-S-R'}} + N_2O + \underset{27}{t\text{-}BuSO_2SBu\text{-}t} \qquad (48)$$

TABLE 11. Deamination of Sulfoximides with t-BuSNO$_2$ in acetonitrile[55]

Sulfoximide R	R'	Yield of sulfoxide (GC)
C_6H_5	C_6H_5	71
p-MeC_6H_4	C_6H_5	85
p-ClC_6H_4	C_6H_5	92
p-$NO_2C_6H_4$	C_6H_5	72

d) Reaction with Carbanions

Oae and Shinhama also reported that reactions of thionitrates 20 and 47 with carbanions give C-alkylthio derivatives, such as sulfides 76 or alkylthio malonates 77 and 78 (Eqs. 49 and 50).[56] These reactions proceed very rapidly even below room temperature.

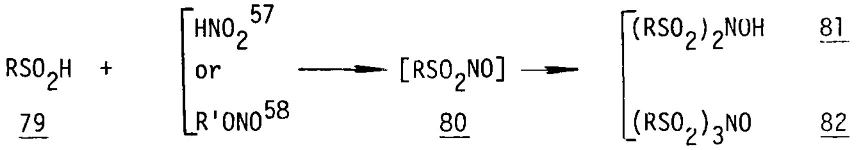
$$\underset{20}{t\text{-}BuSNO_2} + \begin{array}{c} RMgX \\ or \\ RLi \end{array} \xrightarrow{Et_2O} \underset{76}{t\text{-}BuSR} \qquad (49)$$

$$RSNO_2 + CH_2(CO_2Et)_2 \xrightarrow[in\ EtOH]{KOH} \begin{array}{ll} RSCH(CO_2Et)_2 & 77 \\ or & \\ (RS)_2C(CO_2Et)_2 & 78 \end{array} \qquad (50)$$

III. SULFONYL NITRITES

1. Syntheses of Sulfonyl Nitrites

Sulfonyl nitrites 80 have been considered to be intermediates of the reaction of sulfinic acids 79 with nitrous acid[57] or alkyl nitrites (Eq. 51).[58] It has been discovered that sulfonyl nitrites 80 can be isolated in 38-55% yields as brown crystals upon treating sulfinic acids 79 with N_2O_4 (Eq. 52).[2,3]



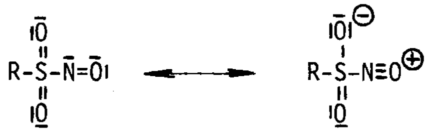
$$\underset{\underline{79}}{RSO_2H} + \left[\begin{array}{l} HNO_2{}^{57} \\ \text{or} \\ R'ONO^{58} \end{array}\right] \longrightarrow \underset{\underline{80}}{[RSO_2NO]} \longrightarrow \left[\begin{array}{ll} (RSO_2)_2NOH & \underline{81} \\ & \\ (RSO_2)_3NO & \underline{82} \end{array}\right] \qquad (51)$$

$$\underline{79} + N_2O_4 \xrightarrow[-20\text{-}0°]{\text{in } Et_2O} RSO_2NO \quad \underline{80} \qquad (52)$$

R; p-Tol, Ph, p-ClC_6H_4, p-BrC_6H_4
p-$MeOC_6H_4$, CH_3

2. Physical Properties of Sulfonyl Nitrites

Most sulfonyl nitrites are unstable brown crystals.[2,3] They show the IR absorption bands of N=O bond at shorter wavelengths (near $1840cm^{-1}$)[2,3] than those of thionitrites ($1490\text{-}1700cm^{-1}$). This is explained in terms of the strong electron-withdrawing effect of sulfonyl groups (Eq. 53), and the SO_2 absorption bands appears near 1390 and $1190cm^{-1}$ in the infrared spectra.[2,3] The mass spectrum of p-toluenesulfonyl nitrite shows the corresponding fragment ion peaks, m/e(rel intensity), 155(9, p-$TolSO_2^+$), 91(20, p-Tol^+), 30(100, NO).[2,3]



80

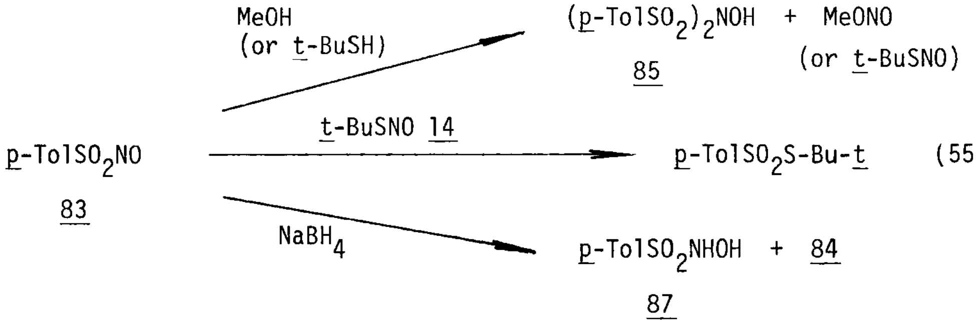
(53)

3. Reactions of Sulfonyl Nitrites

When p-toluenesulfonyl nitrite 83 was heated, evolution of nitrogen oxide gas was observed and white crystals were formed.[2] The physical and spectroscopic data of this substance were identical with those reported as the N-oxide ($(\underline{p}\text{-TolSO}_2)_3\text{N}\rightarrow\text{O}$).[58] However, the spectroscopic data clearly reveals the structure of this compound to be not the N-oxide but instead O-(p-toluenesulfonyl)-N,N-bis(p-toluenesulfonyl)hydroxylamine 84 (Eq. 54).[2]

$$\underset{\underline{83}}{\underline{p}\text{-TolSO}_2\text{NO}} \xrightarrow[\Delta]{\text{in dioxane}} \underset{\underline{84}}{(\underline{p}\text{-TolSO}_2)_2\text{N-O-SO}_2\text{Tol-}\underline{p}} \qquad (54)$$

Sulfonyl nitrite 83 is by far the most powerful nitrosating agent and reacts readily with alcohols or thiols to give corresponding O-nitroso or S-nitroso derivatives along with N,N,-bis(p-toluenesulfonyl)-hydroxylamine 85.[2] Sulfonyl nitrite 83 also reacts with thionitrite 14 to give S-t-butyl p-toluenethiosulfonate 86 in 20% yield.[2] Sulfonyl nitrite 83 is reduced with NaBH_4 to give N-(p-toluenesulfonyl)-hydroxylamine 87 as illustrated in equation (55).[2]



(55)

Sulfonyl nitrite 83 is a powerful nitrosating reagent and hence is an excellent deaminative reagent of aryl amines 55 (Eq. 56).[41] A few typical examples are listed in Table 12.

$$\underset{\underline{55}}{\mathrm{ArNH_2}} + \underset{\underline{83}\ \ 2.4\ \mathrm{eq.}}{\underline{\mathrm{p}}\text{-}\mathrm{TolSO_2NO}} + \mathrm{CuX_2} \xrightarrow[25°,\ 1\ \mathrm{hr}]{\mathrm{in\ CH_3CN}} \underset{\underline{41}\ \mathrm{X;\ Cl,Br}}{\mathrm{ArX}} + \mathrm{N_2} + \underline{85} \qquad (56)$$

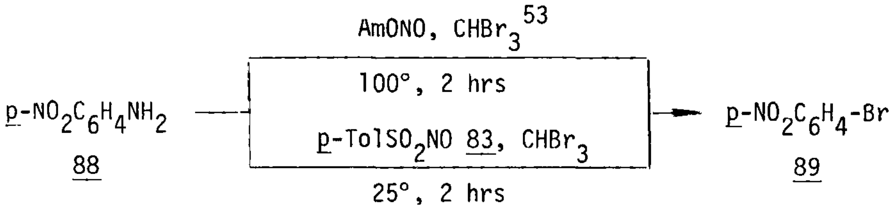
TABLE 12. Deamination of Arylamines with p-TolSO$_2$NO and Anhydrous Copper-(II) Halides at Room Temperature[41]

$ArNH_2$	Yield(by GC) (%)	
	ArCl	ArBr
$\underline{o}$-$NO_2C_6H_4NH_2$	87	63
$\underline{p}$-$NO_2C_6H_4NH_2$	76	79
$\underline{p}$-$BrC_6H_4NH_2$	93	78
$\underline{p}$-$MeOC_6H_4NH_2$	38	60

Sulfonyl nitrite 83 reacts with secondary amine 72 more rapidly than other S or O-nitroso or nitro compounds. N-Nitrosamine 73 is formed within 10 min in a high yield at room temperature (Eq. 57).[38]

$$\underset{\underline{83}}{\underline{\mathrm{p}}\text{-}\mathrm{TolSO_2NO}} + \underset{\underline{72}}{\mathrm{PhNHMe}} \xrightarrow[25°,\ 10\ \mathrm{min},\ 81\%]{\mathrm{in\ dioxane}} \underset{\underline{73}}{\mathrm{PhN(NO)Me}} \qquad (57)$$

Sulfonyl nitrite 83, being the most powerful nitrosating agent, undergoes facile diazo deamination reactions in neutral aprotic solvent even at room temperature without any other catalyst such as copper(II) halides. The results are listed in Table 13. p-Nitroaniline 88 can be converted to p-bromonitrobenzene 89 with sulfonyl nitrite 83 at room temperature for 2 hrs,[38] whereas a similar reaction with amyl nitrite requires heating at 100° (Eq. 57);[53] the yields of bromide 89 are almost the same in both cases.



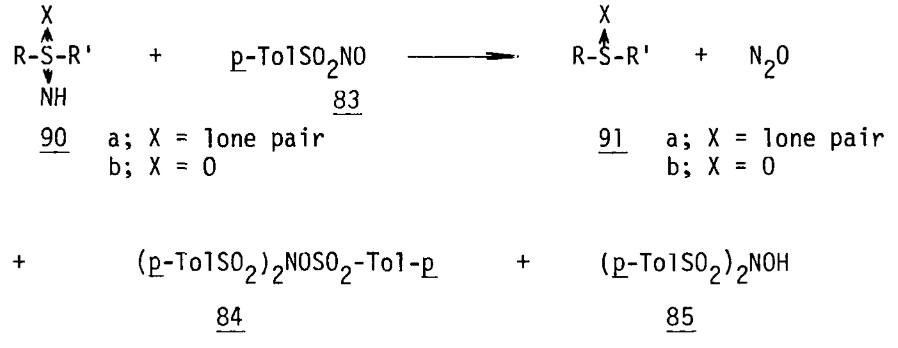
$$\underset{\underline{88}}{p\text{-}NO_2C_6H_4NH_2} \xrightarrow[\substack{p\text{-}TolSO_2NO\ \underline{83},\ CHBr_3 \\ 25°,\ 2\ hrs}]{\substack{AmONO,\ CHBr_3{}^{53} \\ 100°,\ 2\ hrs}} \underset{\underline{89}}{p\text{-}NO_2C_6H_4\text{-}Br} \qquad (58)$$

TABLE 13. Deamination of Arylamines with p-TolSO$_2$NO at Room Temperature[38]

$ArNH_2$	$\frac{[83]^{a)}}{[ArNH_2]}$	Solvent	Reaction Time(min)	Product	Isolated yield(min)
p-BrC$_6$H$_4$NH$_2$	1.5	Benzene	90	p-BrC$_6$H$_4$-Ph	26
p-NO$_2$C$_6$H$_4$NH$_2$	1.9	Benzene	120	p-NO$_2$C$_6$H$_4$-Ph	19
p-NO$_2$C$_6$H$_4$NH$_2$	1.9	$(CH_3)_2S_2$	20	p-NO$_2$C$_6$H$_4$-SCH$_3$	61
p-NO$_2$C$_6$H$_4$NH$_2$	1.9	CHBr$_3$	120	p-NO$_2$C$_6$H$_4$-Br	73

a) Mol ratio.

Reduction of sulfimides 90a and sulfoximides 90b with sulfonyl nitrite 83 also gives nearly quantitative yield of the corresponding sulfides 91a and sulfoxides 91b respectively.[55,59] The reaction requires three equivalents of sulfonyl nitrite 83 to form two side products 84 and 85 as well as 91 (Eq. 58).[55] The results are shown in Table 14.



$$\underset{\underline{90}}{R\text{-}\overset{X}{\underset{NH}{S}}\text{-}R'} + \underset{\underline{83}}{p\text{-}TolSO_2NO} \longrightarrow \underset{\underline{91}}{R\text{-}\overset{X}{S}\text{-}R'} + N_2O$$

90 a; X = lone pair
b; X = O

91 a; X = lone pair
b; X = O

(59)

$$+ \underset{\underline{84}}{(p\text{-}TolSO_2)_2NOSO_2\text{-}Tol\text{-}p} + \underset{\underline{85}}{(p\text{-}TolSO_2)_2NOH}$$

$$\underline{90} + \underline{83} \longrightarrow \underline{91} + p\text{-}TolSO_2H + N_2O$$

$$\underline{p}\text{-TolSO}_2\text{H} + \underline{83} \xrightarrow[\text{fast}]{} \underline{84} + \underline{85} \qquad (60)$$

$$\underline{85} + \underline{83} \xrightarrow[\text{slow}]{} \underline{84}$$

TABLE 14. Deimination of 90 with 3 eq. of 83 at Room Temperature[59]

95			Time (hr)	Solvent	Yield[a)] (%)
R	R'	X			
C_6H_5	C_6H_5	lone pair	1.5	CH_3CN	91
$\underline{o}$-$CH_3OC_6H_4$	C_6H_5	"	"	"	78
C_6H_5	C_6H_5	O	2.0	"	75(78[b)])
$\underline{p}$-$CH_3OC_6H_4$	CH_3	"	"	$CDCl_3$	100[c)]

a) Isolated yield. b) GC yield. c) No other product was detected by NMR.

IV. OTHER USES OF THIONITRITES AND RELATED COMPOUNDS

Various thionitrites and related compounds such as RSNO, $R\overset{O}{\overset{\|}{C}}SNO$, $R\overset{S}{\overset{\|}{C}}SNO$, and $RSNO_2$ were mixed with a hydrocarbon Diesel fuel for improving its ignition properties.[60a,b,c)] Various substances were examined to improve the stability of thionitrites in Diesel fuels.[61a-d)]

t-Butyl thionitrite was also found to be an effective antiscorch agent of rubber similar to butyl nitrite due to their facile fragmentation to form NO and RS radicals.[62]

Morris et al. reported that thionitrites inhibited both germination and outgrowth of B. cereus spores.[63]

The carcinogenicity of these S-nitroso or S-nitro compounds have not been investigated. This should be studies hereafter.

ORGANIC THIONITRITES AND RELATED SUBSTANCES. A REVIEW

SUMMARY

Various uncommon or novel S-nitroso or S-nitro compounds have been prepared and they showed many interesting or unexpected reactions. These compounds were found to be useful agents for diazo deamination reactions in neutral aprotic media. *p*-Toluenesulfonyl nitrite, a new sulfonyl derivative isolated recently, is an especially powerful organic nitrosating agent which undergoes facile diazo deamination or deimination reactions even at room temperature without any catalyst. Furthermore, thionitrites and related compounds were also found to be good starting materials for syntheses of various organic sulfur compounds.

REFERENCES

1. S. Oae, D. Fukushima and Y. H. Kim, Chem. Lett., 279 (1978).
2. S. Oae, K. Shinhama, K. Fujimori and Y. H. Kim, Bull. Chem. Soc. Jpn., 53, 775 (1980).
3. S. Oae, K. Shinhama and Y. H. Kim, Tetrahedron Lett., 3307 (1979).
4. H. S. Tasker and H. O. Jones, J. Chem. Soc., 95, 1910 (1909).
5. H. S. Tasker and H. O. Jones, ibid., 95, 1917 (1909).
6. H. Rheinboldt, Ber., 59, 1311 (1926).
7. H. Rheinboldt, M. Dewaldt and O. Diepenbruck, J. prakt. Chem., 130, 133 (1931); Chem. Abstr., 25, 3618 (1931).
8. J. Mason, J. Chem. Soc., (A), 1587 (1969).
9. H. Lecher and W. Siefker, Ber., 59, 2594 (1926).
10. H. Lecher and W. Siefker, ibid., 59, 1314 (1926).
11. G. Kresze and J. Winlker, Chem. Ber., 96, 1203 (1963).
12. G. Kresze and U. Uhlich, ibid., 92, 1048 (1959).
13. G. T. Walker, Seifen-Öle-Fette-Wachse, 81, 440 (1955); Chem. Abstr., 50, 4641c (1956).

14. D. Vorländer, Ber., 52, 413 (1918).

15. S. Oae, Y. H. Kim, D. Fukushima and T. Takata, Chem. Lett., 893 (1977).

16. S. Oae, D. Fukushima and Y. H. Kim, Chem. Commun., 407 (1977).

17. R. J. Philippe, J. Mol. Spectroscopy, 6, 492 (1961); Chem. Abstr., 55, 19478c (1961).

18. W. L. Fierce, R. L. Weichman, C. Lake and W. J. Sandner (Pure Oil Company), U. S. Pat., 3,134,798 (1964); Chem. Abstr., 61, p4220c (1964).

19. H. Rheinboldt, F. Tappermann and H. Kleu, J. prakt. Chem., 153, 65 (1939); Chem. Abstr., 33, 6279^1 (1939).

20. B. Saville, Analyst, 83, 670 (1958).

21. L. Field, R. V. Dilts, R. Ramanthan, P. G. Lenhert and G. E. Carnahan, Chem. Commun., 249 (1978).

22. P. M. Rao, J. A. Copeck and A. R. Knight, Can. J. Chem., 45, 1369 (1967).

23. A. Holm, N. Harrit and N. H. Toubro, Tetrahedron, 32, 2559 (1976).

24. I. R. Dunkin, M. Poliakoff and J. J. Turner, Tetrahedron Lett., 873 (1976).

25. K. Fuji, K. Ichikawa and E. Fujita, ibid., 3561 (1978).

26. R. J. Philippe and H. Moore, Tobacco Sci., 5, 121 (Pub. in Tobacco 153, 20-3), (1961); Chem. Abstr., 56, 7643g (1962).

27. R. J. Philippe and H. Moore, Spectrochimica Acta, 17, 1004 (1961).

28. R. J. Philippe, J. Mol. Spectroscopy, 6, 492 (1961); Chem. Abstr., 55, 19478c (1961).

29. S. Oae, Y. H. Kim, D. Fukushima and K. Shinhama, J. Chem. Soc., Perkin Trans., 1, 913 (1978).

30. G. W. Ashworth and D. E. Keller, Anal. Chem., 39, 373 (1967); Chem. Abstr., 66, 82191n (1967).

31. R. Bonnett, R. Holleyhead, B. L. Johnson and E. W. Randall, J. Chem.

Soc., Perkin Trans. 1, 2261 (1975).

32. H. Rheinboldt and F. Mott, J. prakt. Chem., 133, 328 (1932); Chem. Abstr., 26, 3775^2 (1932).

33. H. van Zwet and E. C. Kooyman, Rec. Trav. Chim. Pays-Bas, 87, 45 (1968); Chem Abstr., 68, 95426j (1968).

34. J. Barrett, L. J. Fitygibbones, J. Glauser, R. H. Still and P. N. W. Young, Nature, 211, 848 (1966); Chem. Abstr., 65, 19967e (1966).

35. J. Barrett, D. F. Debenhan and J. Glauser, Chem. Commun., 248 (1965).

36. H. Rheinboldt and F. Mott, Ber., 65, 1223 (1932).

37. Y. H. Kim, K. Shinhama, D. Fukushima and S. Oae, Tetrahedron Lett., 1211 (1978).

38. S. Oae et al., Unpublished data.

39. M. Haake, Tetrahedron Lett., 3405 (1972).

40. Y. H. Kim, K. Shinhama and S. Oae, ibid., 4519 (1978).

41. S. Oae, K. Shinhama and Y. H. Kim, Bull. Chem. Soc. Jpn., 53, 1065 (1980).

42. M. P. Doyle, B. Siegfried and J. F. Dellaria, J. Org. Chem., 42, 2426 (1977).

43. M. P. Doyle, B. Siegfried, R. C. Elliot and J. F. Dellaria, ibid., 42, 2431 (1977).

44. Y. H. Kim, K. Shinhama and S. Oae, Bull. Chem. Soc. Jpn., 52, 3117 (1979).

45. S. Oae, K. Shinhama and Y. H. Kim, Chem. Lett., 1077 (1979).

46. R. Adams and W. Reifsneider, Bull. Soc. Chim., France, 23 (1958).

47. D. N. Kramer and R. M. Gamson, J. Org. Chem., 24, 1154 (1959).

48. S. Oae, K. Shinhama and Y. H. Kim, Chem. Lett., 939 (1979).

49. S. Oae, K. Shinhama and Y. H. Kim, Bull. Chem. Soc. Jpn., 53, 2023 (1980).

50. Shu Huang, Hua Hsüeh Hsüeh Pao, 25, 171 (1959); Chem. Abstr., 54,

4489h (1960).

51. M.P. Hassanalv. MM. G. Vernin. H. J. M. Dou and J. Metzger. Bull. Soc. Chem. France. 560 (1974).

52. J. I. G. Cadogan. J. Chem. Soc.. 4257 (1962).

53. J. I. G. Cadogan, D. A. Roy and D. M. Smith, J. Chem. Soc., C, 1249 (1966).

54. L. Friedman and J. F. Chlebowski, J. Org. Chem., 33, 1636 (1968).

55. S. Oae, K. Iida and T. Takata, Phosphorus and Sulfur, 12, 103 (1981).

56. K. Shinhama, Y. H. Kim and S. Oae, Bull. Chem. Soc. Jpn., 53, 1771 (1980).

57. C. S. Marvel and R. S. Johnson, J. Org. Chem., 13, 822 (1948).

58. G. Kresze and W. Kort, Chem. Ber., 94, 2624 (1961).

59. S. Oae, K. Iida and T. Takata, Tetrahedron Lett., 573 (1981).

60. a) E. M. Nygaard, J. H. McCrachen and F. M. Seger (Socony-Vacuum Oil Co.), U. S. Pat., 2,326,102 (1943); Chem. Abstr., 38, p469^7 (1944); b) Standard Oil Development Co., Fr. Pat., 853,052 (1940); Chem. Abstr., 36, p2392^7 (1942); c) R. S. George, G. S. Crandall, E. M. Nygaard and D. E. Badertscher (Socony-Vacuum Oil Co.), U. S. Pat., 2,266,021 (1941); Chem. Abstr., 36, 2392 (1942).

61. a) G. S. Crandall, R. S. George and E. M. Nygaard (Socony-Vacuum Oil Co.), U. S. Pat., 2,328,547 (1943); Chem. Abstr., 38, p1094^6 (1944); b) G. S. Crandall, R. S. George and E. M. Nygaard (Socony-Vacuum Oil Co.), U. S. Pat., 2,328,709 (1943); c) Ibid., 2,328,710 (1943); d) Ibid., 2,328,711 (1943).

62. J. Furukawa, T. Kotani, R. Yamamoto and S. Yamashita, Nippon Gomu Kyokaishi, 33, 270 (1960); Chem. Abstr., 55, 5005c (1961).

63. S. L. Morris, R. A. Levin, W. C. Wright and J. N. Hansen, Spores, 85 (1978); Chem. Abstr., 89, 123689b (1978).

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