Chem. Rev. 1991, 91, 363–373

N-Sulfides. Dinitrogen Sulfide, Thiofulminic Acid, and Nitrile Sulfides

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Received August 3, 1990 (Revised Manuscript Received November 27, 1990)

Contents

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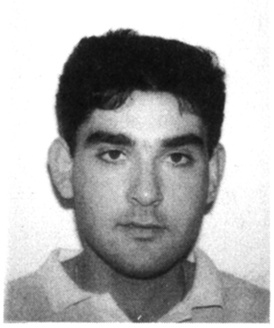

Peter Kambouris was born in Brisbane, Australia in 1966 and commenced study at The University of Queensland in 1984. He received his B.Sc. degree in 1987 and Honours degree in 1988 under the supervision of Prof. C. Wentrup. He is currently completing the requirements for a Ph.D. degree with Prof. C. Wentrup, while investigating sulfur containing reactive intermediates.

I. Introduction

Whereas *N*-oxides (nitrones, nitrile oxides) are well-known compounds showing 1,3-dipolar reactivity,[1] the corresponding *N*-sulfides are extremely unstable and short-lived under usual reaction conditions. N_2O is a particularly stable and unreactive molecule. N_2S, in contrast, is a reactive intermediate which only recently has yielded to direct spectroscopic detection. Fulminic acid (HCNO) and the nitrile oxides[2] are reactive but nonetheless isolable compounds with a long history which in the case of the metal fulminates goes back to the alchemists.[3] The nitrile sulfides have been known as reactive intermediates for only 20 years, and definitive spectroscopic characterization has been achieved only very recently. The HCNO isomers are interesting enough,[4] but in the sulfur series only isothiocyanic acid, HNCS, has been known until this year. HNCS has been identified in the interstellar cloud Sagittarius B2,[5] and since some other sulfur containing species (C_2S and C_3S) show remarkably high abundances in the cold dark cloud TMC-1,[6] one might expect to find the other HCNS isomers as well. Recent advances in the laboratory detection of elusive sulfur containing species[7] including that of thiofulminic acid, HCNS (described below), leave little doubt that the missing isomers (HSCN and HSNC) will also eventually be made.

A review focusing on the chemistry of nitrile sulfides by R. M. Paton was published in 1989.[8] The present review will emphasize mechanistic and spectroscopic aspects.

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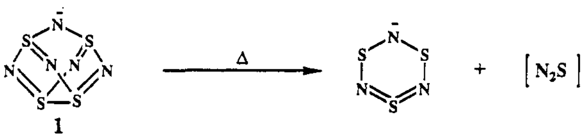
II. Dinitrogen Sulfide, N_2S

A. Background

Powell[9] attributed the carrier of an N_2–CS_2 laser to the linear NNS molecule. It was considered stable and unreactive at room temperature, showing no reaction with charcoal, soda lime, or steel wool, and passing freely through pump oil. It was further considered to be a byproduct of the combustion of coal. It is now known that N_2S is an extremely short-lived molecule, and the carrier of the N_2–CS_2 laser is definitely not NNS.

Linear NNS and the symmetric isomer NSN have also been considered as fragments of the thermal decompositions of various sulfur–nitrogen rings and cages.[10] Thus, the bicyclic ion $S_4N_5^-$ (1) on refluxing in acetonitrile for 6–7 h gives $S_3N_3^-$, formally with elimination of N_2S.[11]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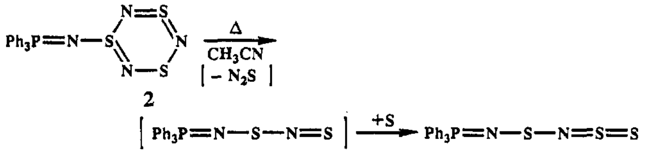
Ab initio calculations[12a] indicated that linear NNS was the lowest energy N_2S species, about 44 kcal/mol below linear N–S–N, but only nitrogen and elemental sulfur were isolated as reaction products. The barrier toward decomposition of linear NSN into N_2 and S was calculated as 15–25 kcal/mol, and for the less stable 90° bent NSN the corresponding barrier was 9–15 kcal/mol.[12a] N_2S has been postulated as a product of the gas-phase reaction between azide ion and CS_2; its heat of formation was estimated as ≤87 kcal/mol, but the molecule was not actually observed.[12b]

The S_3N_3 ring 2 also undergoes thermal fragmentation, formally by elimination of N_2S and capture of a sulfur atom,[13] but mass spectrometric studies of the decomposition of 2 at 100 °C were unable to detect neutral N_2S; only molecular nitrogen and sulfur atoms were detected. This point is of some interest because, as shown below, S_2 molecules would have been expected had NNS been formed.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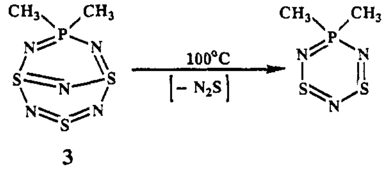
The energy of activation for formal N_2S loss from the $R_2PN_5S_3$ system 3 in toluene solution at ca. 100 °C was determined as ca. 24 kcal/mol, but again no N_2S fragment was detected.[14]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Also the open-chair sulfur diimide 4 undergoes thermal decomposition at 150–160 °C in a closed system, giving decafluoro diphenyl disulfide in 69% yield, but only highly colored unidentified material was reported as accompanying fragmentation products.[15]

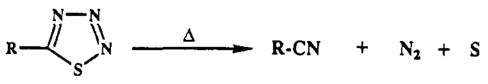
$$C_6F_5{-}S{-}N{=}S{=}N{-}S{-}C_6F_5 \xrightarrow[{[-N_2S]}]{150-160^{\circ}C} C_6F_5{-}S{-}S{-}C_6F_5$$
4

It should be noted that the sulfur dinitride dianion, NSN^{2-}, forms stable salts.[16,17] Ab initio and MNDO calculations indicate a locally stable dianion with an NSN angle of 135°.[18] The dianion of the unsymmetrical NNS is not expected to be stable, however, readily decomposing to N_2 and S^{2-}.[18]

The radical anion $NSN^{\bullet-}$ has been proposed[19] as a product of decomposition of $Ph_3P{=}NS_3N_3$ (2), of $R_2PN_5S_3$ rings, and of sulfur diimides on the basis of ESR measurements, but the sulfur content of the radical was not established and further investigation would be desirable.

B. The Thiatriazole Route

5-Substituted 1,2,3,4-thiatriazoles[20,21] are thermally unstable, decomposing in some cases even at room temperature and sometimes with detonation.[20] 5-Benzylthiatriazole decomposes to benzyl cyanide at room temperature, and the 5-phenyl derivative (5, R = C_6H_5) affords benzonitrile, nitrogen, and sulfur in high yield at 90–100 °C.[22,23] On UV photolysis, a small amount (5–10%) of phenyl isothiocyanate is also formed.[22] The nitrile forming reaction has usually been formulated as a concerted cycloreversion process, yielding sulfur atoms initially:[20–24]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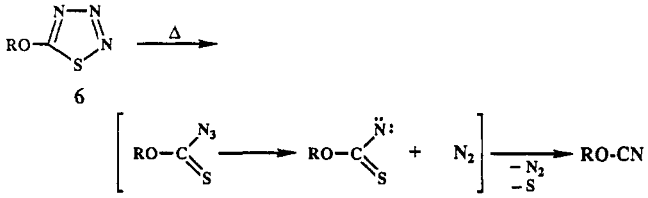
Jensen, Burmester, and Bak (JBB)[25] studied the kinetics of a series of 5-alkoxythiatriazoles (6) in dibutyl phthalate solution and found the reactions to be of first order with very little substituent dependence on the rate. The activation energies were all of the order of 24.6 kcal/mol, and the activation entropies 3.2–4.7 cal/mol K. They considered it plausible that the first step in the reaction involved S–N bond cleavage with the formation of a thio azide, which subsequently (and rapidly) eliminates nitrogen and sulfur, perhaps via a thioacylnitrene intermediate. Attempts to detect the thio azide by IR spectroscopy (expected at ca. 2130 cm^{-1}) were negative.[25] The reaction constitutes a versatile synthesis of alkyl and aryl cyanates.[26]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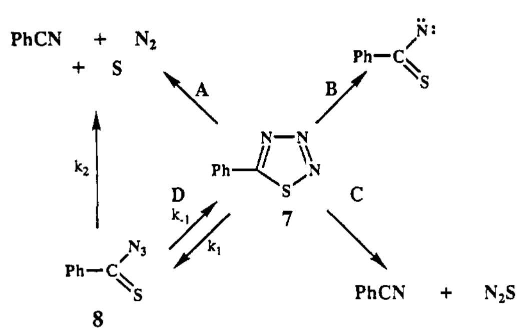
A thorough analysis of the thermal decomposition of 5-phenylthiatriazole (7) was carried out by Holm et al.[27] The activation energy and entropy, measured for the first-order reactions in bromobenzene at 52–61 °C, were 28.2 kcal/mol and 2.8 cal/mol K, respectively. Four possible pathways, A–D, were considered (Scheme I). Paths A and B both involve rate-determining N_2 loss, and since no kinetic isotope effect was observed for the

SCHEME I



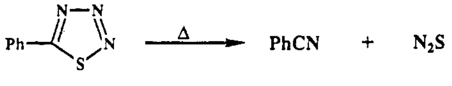
2-^{15}N isotopomer of 7, both of these routes were excluded.

The kinetic isotope effect for the 4-^{15}N isotopomer was ~4%, demonstrating that N_3–N_4 bond breaking is very significant in the transition state. This would be in agreement with either paths C or D, but a search for N_2S (path C) by mass spectrometry was negative. It was concluded that N_2S was not formed, and, in agreement with JBB,[25] pathway D was deemed the only route consonant with the experimental observations. The facts that no thiobenzoyl azide was observable and that only one peak was observed in the differential thermogram required both k_{-1} and $k_2 \gg k_1$. CNDO calculations were in agreement with the expectation that the stable thiatriazole is of lower energy than the thiocarbonyl azide.[28]

It must be pointed out here that the rejection of path C was based essentially on the inability to detect N_2S, and on the erroneous belief of Powell[9] that N_2S would be long-lived. As shown below, path C is indeed operating, and this reaction is a very convenient source of N_2S. Thiobenzoyl azide (8), in contrast, remains unknown.

C. Spectroscopy of N$_2$S

N_2S is produced by flash vacuum pyrolysis of 5-phenyl-1,2,3,4-thiatriazole (7) at temperatures between 300 and 750 °C (10^{-3}–10^{-5} Torr).[29] The yield of N_2S, qualitatively measured by its infrared absorbance relative to that of benzonitrile, critically depends on the contact time in the oven and hence on the oven design. N_2S is stable at 77 K and can be isolated as a neat solid (together with benzonitrile) on the cold end of a liquid nitrogen cryostat or in Ar matrix at 10–20 K by using a closed-cycle liquid helium cryostat. The IR spectrum of N_2S is dominated by a very strong band at 2039 cm^{-1} (neat, 77 K; or Ar, 12 K).

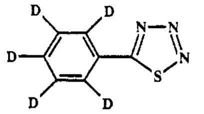


7 (1)

With the pyrolysis apparatus currently in use, the starting material 7 is completely consumed at a pyrolysis temperature well below 700 °C, and absorbance ratios, N_2S:PhCN, as high as 15:1 can be obtained under these conditions. This means that the IR spectrum shows essentially a single, strong line at 2039 cm^{-1}, with a number of much weaker bands which can all be assigned to benzonitrile. With longer contact times, lower oven temperatures will suffice to achieve complete decomposition of 7, but N_2S will also in part decompose to N_2 and sulfur under such conditions.[29]

Once isolated, solid N_2S is stable until 160 K, when the 2039 cm^{-1} absorption disappears, the sample turns opaque, and sulfur is visibly formed. After the sample is warmed to room temperature, benzonitrile and sulfur are isolable in nearly quantitative yields.

The 2039 cm^{-1} feature cannot be due to the compounds Ph-NCS (2047 cm^{-1}), Ph-SCN (2177 cm^{-1}), or Ph-CNS (2185 cm^{-1}; vide infra). It cannot be due to the thio azide 8 either, since 7 is not regenerated on warmup. Furthermore, the thiatriazoles 9–11 all gave the same 2039 cm^{-1} species together with the corresponding nitrile. In the case of 11, N_2S and phenyl cyanate are observed at a pyrolysis temperature as low as 200 °C.



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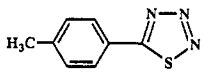

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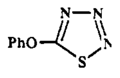

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Ab initio calculations using the HF/6-31G* basis set predict a linear structure of NNS with R_{NN} = 1.086 Å and R_{NS} = 1.652 Å. The predicted stretching fundamentals are ν_{NN} = 2602 cm^{-1} and ν_{NS} = 583 cm^{-1}.[30] Since the 6-31G* basis set typically over estimates vibrational frequencies by a factor 1.12, the observed ν_{NN} frequency of 2039 cm^{-1} is somewhat lower than predicted by theory. The ν_{NS} stretching band, predicted at 583 cm^{-1} and due essentially to an N–S single bond, may similarly be expected in the vicinity of 400 cm^{-1}. This band has not as yet been located experimentally, but all the spectra of N_2S from 7, 9, and 10 feature a second, very weak band at 752 cm^{-1} which shows the same thermal and photochemical behavior as the strong 2039 cm^{-1} band. Both bands are bleached by irradiation with 254 nm light (8–10 h at 10 K). A possible interpretation of the 752 cm^{-1} feature is $2\nu_{NS}$. Current instrumentation does not allow us to observe ν_{NS} itself.

Subsequent to the matrix isolation work,[29] Brown et al.[31] used our method to record the high-resolution gas-phase IR spectrum of N_2S, produced by thermolysis of 7 at 300 °C. The transient N_2S was detectable only by allowing the pyrolyzate to flow through the 16-m pathlength multiple reflexion cell at the maximum pumping capacity of the system. With less-efficient pumping and hence longer contact times, only a broad, featureless absorption due to a stable and unknown molecule was observed; this absorption (2047 cm^{-1}) is evidently not due to N_2S but very likely to a trace of phenyl isothiocyanate, a known byproduct, which absorbs strongly around 2050 cm^{-1} in the gas phase and at 2047 cm^{-1} in matrix. The ν_{NN} stretching fundamental (ν_3) of the transient N_2S gas phase species was observed at 2047.59 cm^{-1}.

Analysis of the fine structure of this band due to the $N_2{}^{34}S$ and $N_2{}^{32}S$ isotopomers afforded the rotational and centrifugal distortion constants and the bond lengths R_{NN} = 1.1388 and R_{NS} = 1.5775 Å in good agreement with MP3/6-31G* calculations. From the equilibrium B value, the N–S bending frequency (ν_2) was calculated as 343 cm^{-1}. Neither ν_2 nor the ν_{NS} stretching vibration (ν_1) were observed directly, and their calculated intensities were significantly less than that of ν_3 at 2047 cm^{-1}.

TABLE I. Experimental Ionization Potentials of N_2S[30]

I_A[a]	I_V[b]	MO ($C_{\infty v}$)	ion state
10.55	10.60	3π	$^2\Pi$
15.36	15.36	9σ	$^2\Sigma$
~15.7	~16.2	2π	$^2\Pi$

[a] Adiabatic. [b] Vertical ionization energy (eV).

TABLE II. Infrared and Ionization Data for Diazonium Betaines[29,30]

compound	ν (cm^{-1})	IP (eV)
$H_2C{=}N^+{=}N^-$	2050	9.0
$H{-}N{=}N^+{=}N^-$	2130	11.5
$O^-{-}N^+{\equiv}N$	2224	12.9
$S^-{-}N^+{\equiv}N$	2039[a]	10.6

[a] Ar matrix value. Gas-phase value:[31] 2047.59 cm^{-1}.

The high-resolution gas-phase IR spectrum proves the structure of N_2S beyond doubt. The composition was also proved by pyrolysis–mass spectrometry.[29] The molecular ion of 7 (m/z 163) almost vanished at 240 °C, whereas that of N_2S (m/z 60) increased in intensity, and its composition was confirmed by high-resolution mass measurement. Interestingly, S_2 is also a pyrolysis product, as seen both in the mass[29] and the photoelectron[30] spectra.

The photoelectron spectrum of N_2S was obtained by pyrolysis of 7 at 310 °C with computer subtraction of bands due to benzonitrile and N_2.[30] The data are summarized in Table I, and the first ionization potentials of the diazonium betaines are compared in Table II. The ionization data for N_2S indicate a relatively weak N–S interaction in the linear N_2S molecule, in agreement with the long N–S bond. The ionization potential as well as the infrared frequency indicate that N_2S is more closely related to CH_2N_2 than to the stable and unreactive N_2O. Peaks due to S_2 were also clearly observed in the spectra, but *monoatomic sulfur was absent*. The temperature dependence of the intensities of N_2S and S_2 peaks indicates that S_2 is a secondary product, arising from N_2S decomposition.

Therefore, the reaction, $N_2S \rightarrow N_2 + S$ can be excluded. Two possible mechanisms for S_2 production are given in eqs 2–3.

$$2NNS \rightarrow \overset{-}{N}{=}N{-}S{-}S{-}\overset{+}{N}{\equiv}N \rightarrow 2N_2 + S_2 \quad (2)$$

$$2NNS \rightarrow N{\equiv}\overset{+}{N}{-}S{-}\overset{-}{S} + N_2 \rightarrow 2N_2 + S_2 \quad (3)$$

Weak signals due to traces of PhNCS were visible in both the infrared, the mass, and the photoelectron spectra, in agreement with the observations of Kirmse[22] and Holm.[27,82]

Photolysis of 7 in an Ar matrix also produces N_2S and benzonitrile as observed by IR spectroscopy.[29] The photoreaction is very slow at 310 nm; it was faster at 254 nm, but prolonged irradiation at this wavelength destroys N_2S. The photoreaction is accompanied by traces of phenyl isothiocyanate.

In summary, the ensemble of spectroscopic properties conclusively proves the identity of N_2S. It is a linear molecule with a rather weak N–S bond. The transient nature of N_2S is not due to inherent thermodynamic instability, however, for there is no evidence for decomposition into N_2 and S_1. The molecule decomposes primarily in a bimolecular process yielding N_2 and S_2. Therefore, high-vacuum and/or low-temperature methods are required to preserve the molecule.

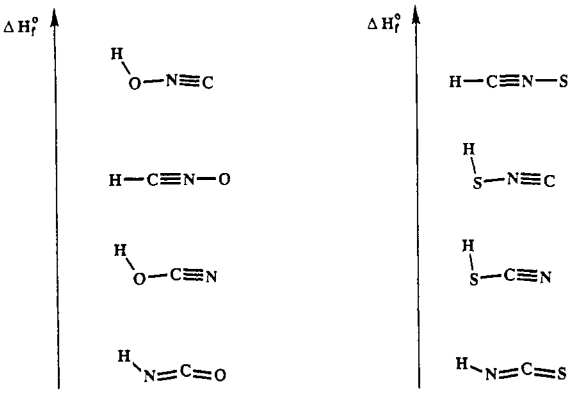


Figure 1. Relative computational energy orderings and approximate geometries of HCNO[4a,g] and HCNS[32] isomers. For experimental geometries of HNCO and HNCS, see: Yamada, J. *J. Mol. Spectrosc.* **1980**, *79*, 323 and Yamada, K.; Winnewiser, M.; Winnewisser, G.; Szalanski, L. B.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1980**, *79*, 295.

III. Thiofulminic Acid, H—C≡N—S

A. Background

Of the four theoretically possible HCNS isomers, only one, isothiocyanic acid HNCS, was previously known. Ab initio calculations[32] indicate that thiofulminic acid, H—C≡N—S, is a linear molecule. It is also the highest energy isomer, in contrast to the HCNO isomers,[4] where isofulminic acid, H—O—NC, is the least stable. The energy orderings are illustrated in Figure 1. HONC[4g] and its esters, R—O—NC,[4f] have recently been characterized by matrix isolation techniques.

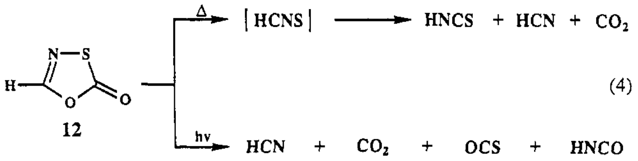
Calculations using the 6-31G* basis set further indicate that CNS and NCS radicals and anions occupy energy minima and that the energy difference between the two is substantially lower than for the CNO/NCO analogues, both in the neutral and the anionic series.[33,34] Vibrational frequencies for the thiofulminate anion, CNS^-, have been calculated; at the Møller–Plesset/2 level, $\nu_1 = 570$; $\nu_2 = 321$; $\nu_3 = 2109$ cm^{-1}.[34]

It is believed that substances containing thiofulminate ligands are formed in the reaction between potassium hexacyanoferrate(III) and molten sulfur at 200 °C.[35] This interpretation is due largely to infrared spectroscopy, the compounds showing very strong absorptions at 2071–2025 cm^{-1}. However, the assignment of strong bands at 1215–1108 cm^{-1} to the N–S stretching vibration on the basis of analogy with the N–O stretch at 1205–1050 cm^{-1} in fulminate ligands seems dubious and is in disaccord with the above calculations[34] for the thiofulminate anion.

B. Detection of Thiofulminic Acid

Attempts by Bak et al.[32] to observe HCNS by pyrolysis and photolysis of 1,3,4-oxathiazol-2-one (**12**) were not encouraging.

Only isothiocyanic acid (HNCS), CO_2, and HCN were observed by microwave and mass spectrometry in the thermal process (700 °C, 2.10^{-2} Torr), and HCN, CO_2, OCS, and HNCO in the photochemical process. The same products were obtained on gas-phase irradiation with a CO_2 laser operating at 10.5 μm.[62]



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Nevertheless, we have used **12** to obtain the first direct evidence for the existence of neutral H—C≡N—S by using neutralization–reionization mass spectrometry (NRMS).[37] In this technique[36] a beam of mass-selected ions is neutralized in a collision cell by colliding it with Xe and then reionized in a second collision cell by collision with O_2. The recovery of a mass spectrum of the resulting ions implies the existence of the corresponding neutral molecules with lifetimes of the order of at least 0.5 μs.

The collision–activation mass spectrum (CAMS) of isothiocyanic acid (HNCS) is characterized by signals at m/z 27 (HCN), 32 (S), and 44 (CS). The CAMS of the mass-selected m/z 59 ions (M − CO_2) emanating from the electron ionization (EI) mass spectrum of oxathiazolone **12** also shows signals at m/z 27 and 32, but differs from that of HNCS by an intense peak at m/z 46 (NS). This clear differentiation demonstrates that the m/z 59 ion formed by fragmentation of $\mathbf{12}^{\bullet+}$ has the structure $H{-}C{\equiv}N{-}S^{\bullet+}$.

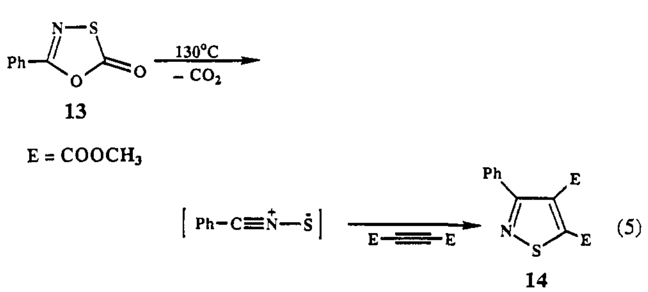
The NRMS of $H{-}N{=}C{=}S^{\bullet+}$ regenerates, as expected, a mass spectrum identical with the original CAMS of this ion. The NRMS of the m/z 59 ions from $\mathbf{12}^{\bullet+}$ likewise regenerates a strong survivor signal at m/z 59, with a spectrum identical with the original one, and in particular still showing the characteristic m/z 46 (NS) signal. Thus, neutral H—C≡N—S does not isomerize to H—N═C═S to any significant extent on the microsecond time scale of this experiment.[37]

IV. Nitrile Sulfides, RCNS

A. Generation and Trapping Reactions

1. From 1,3,4-Oxathiazol-2-ones

Benzonitrile sulfide was first generated by Franz and Black[38] by thermolysis of 4-phenyl-1,3,4-oxathiazol-2-one (**13**) in chlorobenzene at 130 °C and trapped in a 1,3-dipolar cycloaddition reaction with dimethyl acetylenedicarboxylate in over 90% yield.



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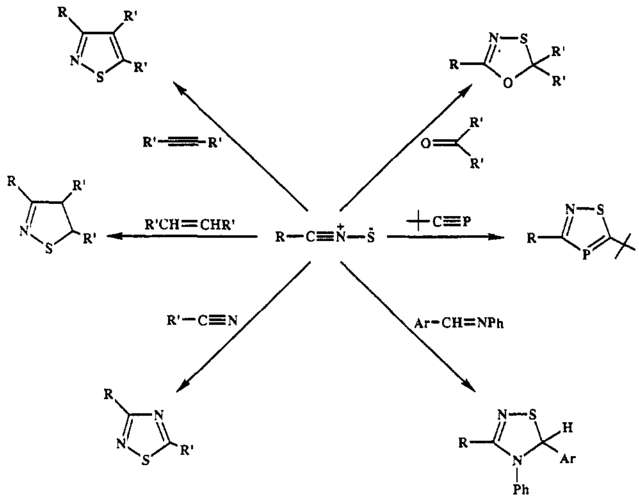
SCHEME II



Oxathiazolones of the type **13** had first been prepared by Senning[39] and by Muhlbauer and Weiss,[40] and Senning had noted that "pyrolysis" resulted in the nitrile, CO_2, and sulfur. This is a common observation: in the absence of a dipolarophile, or with inefficient dipolarophiles, the nitrile sulfide decomposes to the nitrile and sulfur. As in the case of N_2S, we do not expect this to be a unimolecular process with monoatomic sulfur formation:

$$R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{S} \longrightarrow R{-}C{\equiv}N + \text{"S"} \qquad (6)$$

We shall return to this point in section C.

Kinetic studies of the reaction shown in eq 5 were in agreement with rate-determining formation of the nitrile sulfide intermediate and excluded the possibility of a direct reaction between **13** and the trapping agent.[41]

In further work, nitrile sulfides have been added to a variety of electron poor acetylenes,[42,43] electron poor or strained (norbornene) alkenes,[44,45] and to the CC double bond in *p*-quinones.[46] Intramolecular addition to electrophilic CC triple bonds also occurs with formation of bicyclic isothiazoles in good yields.[47] Intramolecular addition to CC double bonds is less efficient and results in secondary reactions.[47] The addition to CC multiple bonds has been utilized in the modification of unsaturated polymers by cross-linking with arylene bis(nitrile sulfides)[48] and in the production of polymers from copolymer-bound oxathiazolones which on heating generate nitrile sulfides that can be trapped with dimethyl acetylenedicarboxylate, ethyl propiolate, diethyl fumarate, etc.[49]

Aromatic nitrile sulfides add efficiently to the CN triple bond in electrophilic nitriles such as ethyl cyanoformate,[50,51] aromatic nitriles,[52,53] trichloroacetonitrile,[54] and acyl cyanides[55] and in aryl thiocyanates and selenocyanates.[56] Likewise, addition takes place to the CN group in tetracyanoethylene and not to the CC double bond.[57] Benzonitrile sulfide also adds to the CP triple bond in *tert*-butylphosphaacetylene to give a 1,2,4-thiazaphosphole in 82% yield.[58]

Reaction with imines (Schiff's bases of aromatic aldehydes) gives only poor yields of cycloadducts.[59] Perhaps more electrophilic imines should be investigated. Cycloaddition with electronegatively substituted aldehydes and ketones, such as chloral, hexachloroacetone, and trifluoroacetophenone yields 1,3,4-oxathiazoles in modest to good yields.[60]

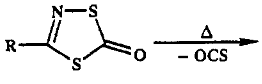
1,4,2-Dithiazoles are similarly obtained in 10–65% yield by cycloaddition to the CS double bond in alkyl aryl thioketones and in *O*-ethyl thiobenzoate.[61]

The various reaction types are illustrated in Scheme II and further preparative details are given in Paton's review.[8] It is usually advantageous to add the oxathiazolone precursor slowly to the hot solution of the dipolarophile in order to maintain a low concentration of nitrile sulfide and a high reaction temperature. Yields are increased by low solvent polarity, for example by adding dodecane as a diluent.[53] While most studies have been carried out with aromatic nitrile sulfides, also alkyl (e.g. CH_3CNS,[42,57,60] *tert*-C_4H_9CNS[62]), vinyl[49,62] dimethylamino (Me_2N-CNS[55]), and 5-β-D-ribofuranosyl[51] substituents have been employed.

It is a general observation that these cycloadditions are favored by electropositive substituents in the nitrile sulfide and by electronegative ones in the dipolarophile. In other words, the reactions are dominated by HOMO (dipole) LUMO (dipolarophile) interactions.[52,63] In this regard, the nitrile sulfides are more closely related to nitrile ylides than to nitriles imines or nitrile oxides. In the latter two classes of nitrilium betaines both HOMO (dipole)–LUMO (dipolarophile) and LUMO (dipole)–HOMO (dipolarophile) interactions are important.[64] This is similar to the conclusion reached for N_2S (section II) which is more like diazomethane than HN_3 or N_2O.

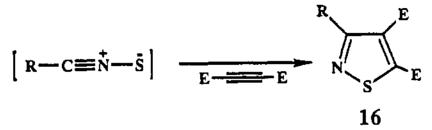
2. From 1,3,4-Dithiazol-2-ones

The dithiazolones 15 are more stable than oxathiazolones 13 but decompose to nitrile sulfides in boiling mesitylene (160 °C). The nitrile sulfides (R = CH_3 or C_6H_5) were trapped with dimethyl acetylenedicarboxylate in 56 and 52% yields, respectively.[65]



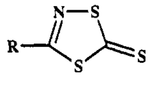
15

R = CH_3 or C_6H_5
E = $COOCH_3$



16

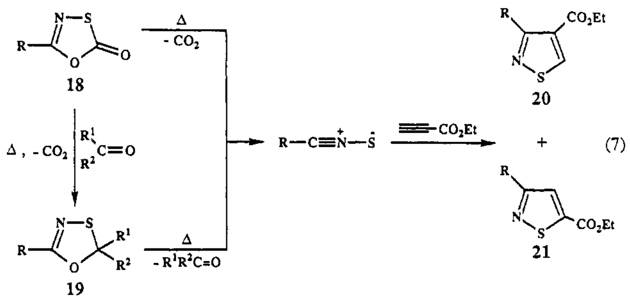
The corresponding dithiazolethiones 17 give low yields of 16 on photolysis,[66] but the thermal reaction takes a different course, and thus 17 is not a preparatively useful nitrile sulfide source.[67]



17

3. From 1,3,4-Oxathiazoles and 4,5-Dihydro-1,2,4-thiadiazoles

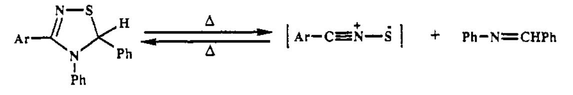
Oxathiazoles 19, themselves obtained from nitrile sulfides and electron-poor aldehydes or ketones, are useful thermal precursors of nitrile sulfides at temperatures around 160 °C. Since variously substituted oxathiazoles can be prepared (e.g. $R^1 = R^2 = CCl_3$; $R^1 = C_6H_5$, $R^2 = CF_3$; $R^1 = CCl_3$, $R^2 = H$), it was possible to probe the occurrence of a common intermediate, viz. the nitrile sulfide, from three different oxathiazoles 19 as well as oxathiazolone 18. The observation of almost identical ratios (1.325 ± 0.015) of the 4- and 5-(ethoxycarbonyl)-3-(*p*-methoxyphenyl)isothiazoles (20 and 21) formed with ethyl propiolate is strong evidence that all these reactions proceed via the discrete nitrile sulfide intermediate.[68,69]



(7)

R = p-CH_3O-C_6H_5

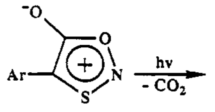
The 4,5-dihydro-1,2,4-thiadiazoles 22, obtained from oxathiazolones and imines (Scheme II), undergo an analogous cycloreversion to nitrile sulfides, which are trappable with dimethyl acetylenedicarboxylate and ethyl cyanoformate.[59]



22

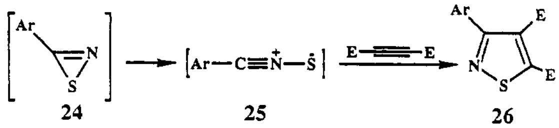
4. From 1,3,2-Oxathiazolio 5-Oxides

Gotthardt[70] found that solution photolysis (450-W medium-pressure Hg lamp; λ > 395 nm or λ = 405–408 nm) of 4-aryl-1,3,2-oxathiazolio 5-oxides 23 in the presence of dimethyl acetylenedicarboxylate led to nitrile sulfide cycloadducts 26 in yields varying from 0 to 31%. Tetramethyl thiophenetetracarboxylate was formed as well and is a known product of reaction of the acetylene with elemental sulfur. In the absence of a trapping agent, benzonitrile (77%) and sulfur (>90%) were obtained from the 4-phenyl compound. It was suggested that the thiazirine 24 and the nitrile sulfide 25 were reactive intermediates.



23

E = $COOCH_3$

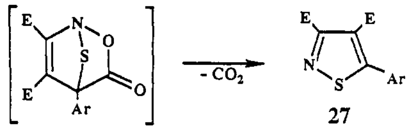


24 25 26

The thermal reaction between 23 and acetylene dicarboxylate at 85–95 °C took a different course, involving direct cycloaddition to 23 followed by CO_2 elimination to give the isomeric isothiazole 27.[71]

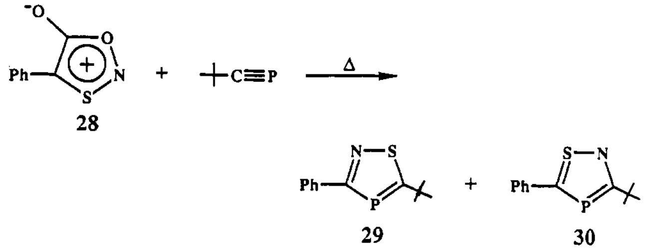
$$23 + E{\equiv}E \xrightarrow{\Delta}$$

E = $COOCH_3$



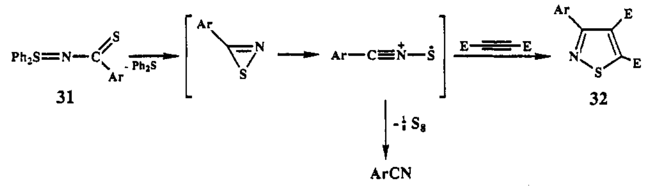
27

However, the thermal reaction of 28 with *tert*-butylphosphaacetylene in benzene solution at 80 °C has been reported to give a 1:9 mixture of the isomeric cycloadducts **29** and **30**, thereby indicating that nitrile sulfide formation from **28** can also take place thermally.[72]



5. From N-(Thiocarbonyl)-S,S-diphenylsulfimides

An interesting reaction is reported for the sulfimides **31** which, at temperatures as low as 70 °C decompose to nitrile and sulfur, and in the presence of dimethyl acetylenedicarboxylate give the expected trapping product of a nitrile sulfide **32**. Analogous products were obtained with other alkynes.[73a] The combined yield of nitrile and **32** was quantitative. The reaction was first order, and the rate of appearance of the nitrile was independent of the presence or absence of the alkyne, and also the rate of appearance of **32** was independent of the alkyne concentration but highly dependent on the electrophilicity of the alkyne. It was assumed that the nitrile sulfide was in rapid equilibrium with the thiazirine and that the latter was the source of ArCN and sulfur. This is in disagreement with other work, which has demonstrated sulfur loss from nitrile sulfides (see section IV.C), and suggests, therefore, that there is an independent route to ArCN from **31**.[73b] The reaction seems worthy of further investigation.



6. From (Alkylimino)sulfur Difluorides

Aromatic and aliphatic nitrile sulfides have been generated by fluoride ion induced HF elimination from iminosulfur difluorides **33**.[63] The nitrile sulfides have been trapped with acetylenic esters and by addition to the CC double bond in quinones and in *N*-phenylmaleimide.[63,74]

$$\underset{\mathbf{33}}{R{-}CH_2{-}N{=}SF_2} \xrightarrow[132^\circ C]{2\,NaF} [R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{S}]$$

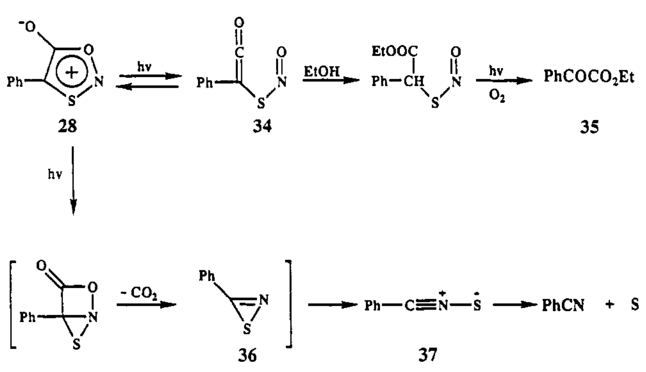
R = C_6H_5; CH_3; CF_3

7. From Thioamides and Related Compounds

Nitrile sulfides have been invoked in a variety of oxidative reactions of aromatic thioamides.[75-76] In most cases there is little or no decisive evidence for the actual involvement of a nitrile sulfide, and in at least one case the nitrile sulfide was deemed not to be involved.[77]

It has also been suggested[78] that nitrile sulfides may be involved in the formation of so-called abnormal products (cyanoalkyl episulfides) of catabolism of glucosinolate anions (thiohydroximate *O*-sulfonates).

SCHEME III

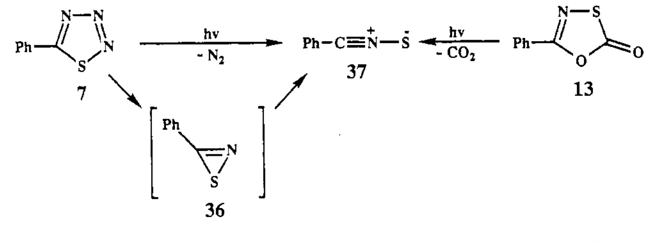


B. Direct Observation

1. UV Spectroscopy

Holm et al.[79] examined the photolysis of 4-phenyl-1,3,2-oxathiazolio 5-oxide (**28**) in an EPA glass at 85 K by UV spectroscopy. Irradiation with 420 ± 13 nm light caused the appearance of two intermediates, assigned as the ketene **34** (λ_{max} 324 nm) and benzonitrile sulfide (**37**) (λ_{max} 335, 313, 295, 240 nm) (Scheme III). Irradiation with 335 ± 14 nm light caused disappearance of these intermediates, whereby **34** disappeared more slowly. **34** was trapped in separate experiments by photolysis in ethanol solution, giving a 65% yield of ethyl phenylglyoxylate (**35**) together with 21% of benzonitrile.[79,80] Warming of the EPA glass containing **34** and **37** to room temperature also resulted in benzonitrile formation.[79] The EPA glass at 77 K did not contain any radicals according to ESR spectroscopy, but prolonged irradiation at 335 nm caused appearance of an ESR signal ascribed to an RS• radical, presumably the thiyl formed by NO elimination from **34**.[79,81]

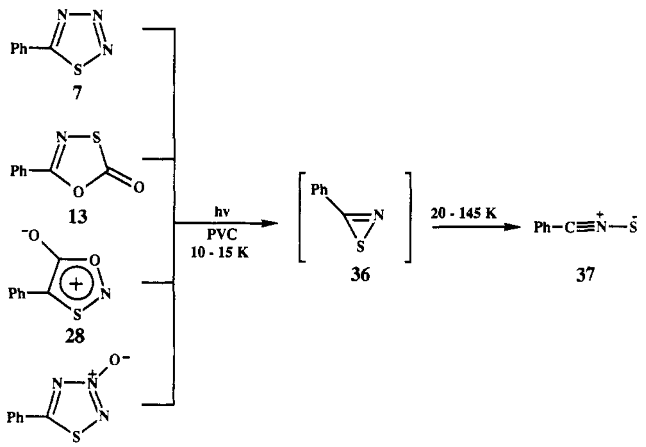
It was subsequently found that the same UV absorptions ascribed to benzonitrile sulfide (**37**) were also generated by photolysis of both phenylthiatriazole (**7**) and phenyloxathiazolone (**13**) in EPA glass at 85 K.[82] Room temperature photolysis in the presence of dimethyl acetylenedicarboxylate resulted in a 9% yield of cycloadduct from **7**, and 22% from **13**. Thus, remarkably, at least *some* nitrile sulfide **37** is formed on photolysis of **7**, whereas the thermal reaction gives largely N_2S (section II). Ar matrix photolysis of **7** also gives N_2S albeit in small amount (section II) and no PhCNS, and liquid-phase photolysis gives phenyl isothiocyanate in ca. 7% yield.[22,82]



In spite of the complexities, it seems clear that **37** is formed, and the reaction is assumed to occur via the thiazirine **36**. No ESR active species such as thiobenzoylnitrene was detectable.

Evidence for the initial formation of thiazirine **36** as a common intermediate was adduced from photolysis of several precursors (Scheme IV) in PVC film at 10–15 K.[83] Although no discrete UV bands could be assigned

SCHEME IV



to the low-temperature intermediate, warming of the samples from 20 to 145 K resulted in the appearance of the UV spectrum of benzonitrile sulfide (**37**), the absorptions growing in a stepwise fashion (Scheme IV). The UV spectrum of **37** can be observed in the PVC film even after warming to room temperature. The dithiazolethione **17** (R = C_6H_5) did not, however, give any benzonitrile sulfide on such treatment. All the precursors in Scheme IV as well as thione **17** and several other heterocyclic compounds afforded the nitrile sulfide cycloaddition product with dimethyl acetylenedicarboxylate in yields of 5–21% on liquid-phase photolysis at room temperature.[66]

2. IR Spectroscopy

The observations made by UV spectroscopy have been correlated with IR spectroscopy in N_2 matrix and in PVC film.[81] Broadly, the mechanism given in Scheme III is confirmed. The nitrosothio ketene **34** absorbs at 2100 cm^{-1} in PVC film and at 2115 cm^{-1} in N_2 matrix. It is in photoequilibrium with the starting material **28**, exists in *Z* and *E* forms, and on further photolysis is cleaved into a thiyl radical.

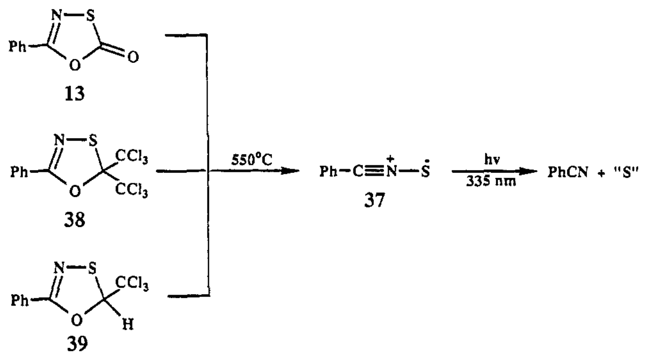
The nitrile sulfide **37** is *not* observed in N_2 matrix, but in PVC film at 80–85 K it absorbs at 2185 cm^{-1}. **37** is formed by irradiation of the precursor **28** in the film at 470 nm, i.e. the edge of the absorption band, and it appears before bands due to benzonitrile. **37** is bleached by photolysis into its UV maximum at 335 nm. Warmup caused **37** to disappear at ca. −60 °C (but being observable up to room temperature in PVC under certain conditions), and the temperature profile for disappearance was the same as that established by UV spectroscopy.

No other valence tautomer of the oxathiazolio 5-oxide **28** was observed by IR (or UV) spectroscopy, nor was thiazirine **36** apparent in the IR (or UV) spectra.

While these studies established the existence and properties of benzonitrile sulfide without doubt, there still was no direct evidence for nitrile sulfides in thermal reactions, especially in the preparatively most versatile thermolyses of oxathiazolones and oxathiazoles (eqs 5 and 7).

We therefore embarked on an Ar matrix isolation study of the flash vacuum pyrolysis products of the precursors **13**, **38**, and **39** (Scheme V).[37,84] Pyrolysis of **13** at 550 °C with Ar matrix isolation at 20 K produced CO_2, benzonitrile, and a species absorbing at 2185 cm^{-1}.

SCHEME V



Since **37** decomposes thermally to benzonitrile and sulfur, it is not possible to obtain a large amount of **37** in this way. The best ratio of the absorbances of benzonitrile and **37** was 3.6:1. Photolysis of this matrix with 335-nm light caused disappearance of the 2185 cm^{-1} absorption with a concomitant slight increase in the benzonitrile absorption clearly seen in the difference spectrum. The hexachloroacetone derivative **38** was an even better precursor of benzonitrile sulfide under identical conditions, and again the 2185 cm^{-1} species was bleached with 335 nm light. Careful evaporation of the Ar at >50 K also caused the 2185 cm^{-1} peak to vanish. The cloral derivative **39** was a poorer precursor of **37**, giving a weak signal at 2185 cm^{-1} together with benzonitrile, chloral, and dichloro ketene.

These results make it clear that benzonitrile sulfide is a discrete intermediate in both the photochemical and the thermal processes. It is perhaps a priori surprising that it survives flash pyrolyses at temperatures above 500 °C, although the yield of the trapped nitrile sulfide is definitely low. Further proof of the identity of the gas-phase species was obtained by mass spectrometry.[37]

Acetonitrile sulfide, $CH_3—C≡N—S$, was identified by IR spectroscopy in a similar manner (2230 cm^{-1}).[37] The higher frequency vis-à-vis $Ph—C≡N—S$ is in accord with the higher frequencies of CH_3NCS, CH_3SCN, and CH_3CN with respect to the phenyl analogues. The 2230 cm^{-1} species was again bleached by short wavelength light. The proof of its composition was given by mass spectrometry (see below).

3. Mass Spectrometry

The EI mass spectrum of **13** shows the molecular ion (*m/z* 179), a weak signal corresponding to benzonitrile sulfide (*m/z* 135), and a weak one due to benzonitrile (*m/z* 103). The base peak is *m/z* 105, corresponding to $PhCO^+$. Pyrolysis above 200 °C causes the molecular ion and $PhCO^+$ to disappear, and the benzonitrile ion becomes the base peak. CO_2 appears at the same time, and there is a small increase in the signal due to S_2 at *m/z* 64, whose composition was determined by high-resolution mass measurement. There was no definite increase in the already weak signal due to PhCNS at *m/z* 135, indicating that PhCNS may decompose thermally at a rate similar to that of its formation. This ion was still detectable at 500 °C, however.[85]

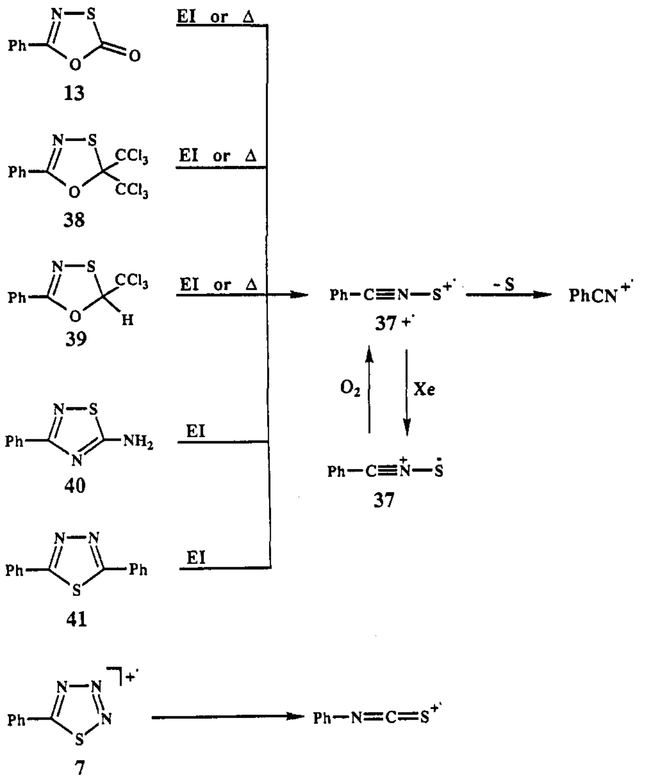
The hexachloroacetone derivative **38** again proved to be the best thermal precursor. Although the intensity of the *m/z* 135 ion (PhCNS) decreased over the temperature range 100–500 °C, the intensity decrease was less rapid above 270 °C, and from 300 °C onward this

TABLE III. Collision Activation Mass Spectra of m/z 135 $C_7H_5NS^{\bullet+}$ Ions[85]

	m/z, relative abundances[a]												
precursors	108	103	91	90	84	82	77	76	69	63	58	51	50
7	(340)	(90)	(200)	64	(30)	17	(*1140*)	22	15	35	5	*100*	52
13	(200)	(*465*)	(129)	45	(18)	13	(356)	*100*	16	32	5	52	39
38	(197)	(*448*)	(121)	43	(14)	11	(310)	*100*	14	32	6	52	43
39	(202)	(*406*)	(127)	40	(15)	8	(333)	*100*	11	28	4	50	41
40	(179)	(*149*)	(110)	42	(15)	10	(317)	*100*	11	27	4	47	36
41	(293)	(*445*)	(164)	55	(19)	13	(*500*)	*100*	13	29	3	58	39
PhNCS	(126)	(40)	(87)	59	(14)	14	(*720*)	17	14	32	5	*100*	49
PhSCN	(1192)	(23)	(569)	95	(85)	39	(454)	54	69	49	18	*100*	67

[a] Abundances relative to the most intense collision induced peak excluding unimolecular processes which are noted in parentheses.

SCHEME VI



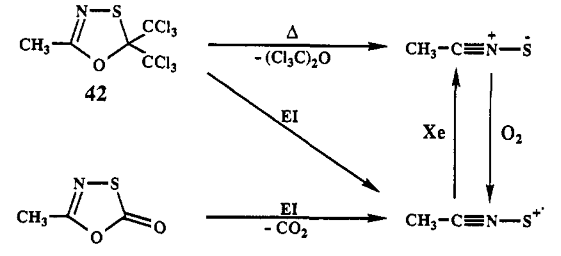
signal became relatively stronger than those due to the rapidly disappearing starting material **38**. The signal due to S_2 increased over the whole temperature range, and benzonitrile (m/z 103) became the base peak from 220 °C onward.

The identity of the m/z 135 ion as the molecular ion of benzonitrile sulfide (**37**) was established for several different precursors (Scheme VI) by using kinetic energy, metastable ion, collision activation (CA), and neutralization-reionization (NR) mass spectrometry. In particular, the CA spectrum of **37** is characterized by a very strong loss of S_1. The molecular ion of Ph—C≡N—S (m/z 135) is readily distinguished from those of Ph—N=C=S and Ph—S—C≡N (Table III). Note that the m/z 135 ion from phenylthiatriazole (**7**) is due to Ph—N=C=$S^{\bullet+}$, not Ph—C≡N—$S^{\bullet+}$ (Scheme VI).

The proof that the neutral Ph—C≡N—S (**37**) also exists in the gas phase and has the same structure as the ion Ph—C≡N—$S^{\bullet+}$ was given by NRMS of m/z 135 produced from **13** and **40**. These spectra clearly showed survivor signals at m/z 135, with the characteristic sulfur loss to give m/z 103.[85,37]

In like manner, acetonitrile sulfide was observed by matrix isolation IR spectroscopy at 2230 cm^{-1} as formed by flash vacuum pyrolysis of **42** at 300–500 °C. The oxathiazolone **43** gave no comparable signal under similar conditions[37] (Scheme VII).

SCHEME VII



The EI mass spectra of **42** and **43** also show abundant ions due to CH_3—C≡N—S (m/z 73) (100% in the case of **42**; 10% in the case of **43**). The structure CH_3—C≡N—$S^{\bullet+}$ was established by differentiation of the kinetic energy, metastable ion (MI), and CA mass spectra from those of the isomeric CH_3—N=C=S and CH_3—S—C≡N ions. The CAMS of $CH_3NCS^{\bullet+}$ is characterized by a signal at m/z 44 (CS); that of $CH_3SCN^{\bullet+}$ by a loss of HCN (to m/z 46); and that of CH_3—C≡N—$S^{\bullet+}$ by signals due to NS and HNS (m/z 46, 47). Both $CH_3NCS^{\bullet+}$ and $CH_3SCN^{\bullet+}$ show strong losses of one hydrogen atom in the MI spectra, a fragmentation which is absent for CH_3—C≡N—$S^{\bullet+}$. Likewise, these ions have very different kinetic energy release profiles.[37]

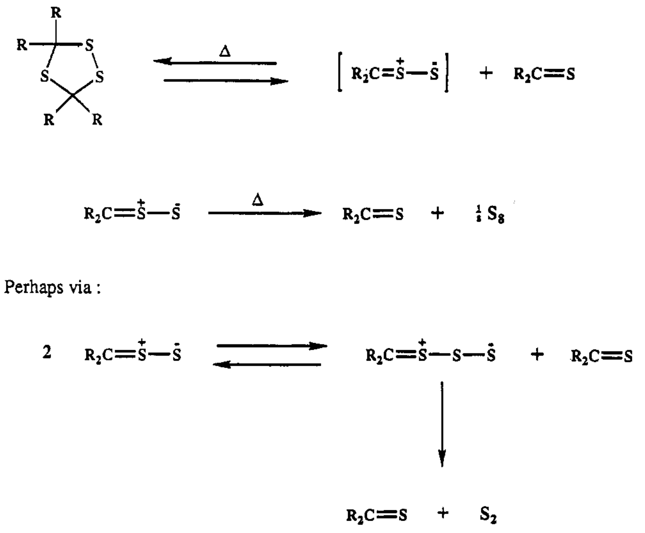
Finally, NRMS with Xe/O_2 resulted in a survivor signal for CH_3—C≡N—$S^{\bullet+}$, originally formed by dissociation of **43**$^{\bullet+}$. The NRMS of CH_3—C≡N—S showed the same characteristics as the CA spectrum and was again distinguishable from the NRMS of CH_3NCS and CH_3SCN. Thus, the existence of neutral CH_3—C≡N—S molecules with lifetimes of at least microseconds in the gas phase is established.[37]

C. Mechanism of Sulfur Loss from Nitrile Sulfides

As mentioned above, matrix-isolated aromatic nitrile sulfides usually decompose to the nitrile and sulfur on warming to ca. 140 K, except in the rigid PVC matrix, where they are observable for short periods at room temperature.[82]

It has long been realized that the liquid-phase decomposition of benzonitrile sulfide is not a simple unimolecular reaction.[53,68,87] Howe and Shelton[53] suggested that the decomposition is accelerated by reaction with short sulfur chains (S_1 to S_7), i.e. by a sulfur-transfer reaction. Holm et al.[87] demonstrated pseudo-first-order decay rates in highly dilute (10^{-5}–10^{-6} M)

SCHEME VIII



ethanolic solutions at room temperature (lifetimes ~1 ms; E_a ~4.3 kcal/mol; $\Delta S^{\ddagger}$ ~30 cal K^{-1} mol^{-1}). The decay rates were 3–4 times slower in a less polar solvent (CCl_4), and deviation from first-order kinetics was observed here. A direct involvement of ethanol in the transition state would give rise to the pseudo-first-order kinetics observed in that solvent. The sulfur was expected to be extruded initially as S atoms, but reactions between RCNS and S, giving S_2, would cause higher-order kinetics, and this would be more dramatically evident in concentrated solutions.

If the activation energy for unimolecular decomposition was only ca. 4 kcal/mol, we would not expect to be able to matrix isolate nitrile sulfides formed in flash vacuum pyrolysis reactions.

In all the pyrolysis–mass spectrometry studies we see S_2 (m/z 64) increasing in intensity with the temperature. In the purely mass spectrometric unimolecular reactions, loss of atomic S is, of course, seen from the $R{-}C{\equiv}N{-}S^{\bullet+}$ ions. In the case of $CH_3{-}C{\equiv}N{-}S^{\bullet+}$ produced from either $\mathbf{42}^{\bullet+}$ or $\mathbf{43}^{\bullet+}$ (Scheme VII), there is a very marked increase in the S_2 signal at the onset of pyrolysis (250–400 °C). At the same time, the molecular ions ($\mathbf{42}^{\bullet+}$ and $\mathbf{43}^{\bullet+}$) disappear, and the S_1 signals (m/z 32) are greatly reduced as less acetonitrile sulfide arrives at the ion source due to thermal fragmentation.[37,86]

Therefore, in analogy with the N_2S case (section II) we tentatively suggest S_2 formation via dimerization or (more likely) sulfur atom transfer mechanisms:

$$2R{-}CNS \rightarrow [R{-}\overset{-}{C}{=}N{-}S{-}S{-}\overset{+}{N}{\equiv}C{-}R] \rightarrow 2RCN + S_2$$

$$2R{-}CNS \rightarrow [R{-}C{\equiv}\overset{+}{N}{-}S{-}\overset{-}{S}] + RCN \rightarrow 2RCN + S_2$$

There are many other reactive sulfur species that may decay via sulfur atom transfer and S_2 formation, e.g. the thione *S*-sulfides reported by Huisgen et al.[88] for which a mechanism is suggested in Scheme VIII. The powerful modern mass spectrometric techniques would seem to be best suited for investigations of such reactions in the gas phase. Solution-phase studies will be complicated by the instability of S_2 and other short sulfur chains.

Registry No. N_2S, 56400-02-3; HCNS, 65195-59-7.

V. References

(1) Padwa, A., Ed. *1,3-Dipolar Cycloaddition Chemistry*; John Wiley & Sons: New York, 1984; Vols. 1 and 2.

(2) Grundmann, C.; Grünanger, P. *The Nitrile Oxides*, Springer-Verlag: Heidelberg, 1971.

(3) (a) Mercury fulminate was prepared by C. Drebbel (1572–1634) and J. Kunckel von Löwenstern (1630–1703).[2,3b] The publication by Howard in the year 1800 was the first scientific description of this salt.[3c] (b) Kirk, R.; Othmer, D. F. In *Encyclopedia of Chemical Technology*; Interscience Encyclopedia: New York, 1951; Vol. 6, p. 10. (c) Howard, E. *Phil. Trans. Roy. Soc. London* **1800**, 204.

(4) (a) Poppinger, D.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 7806. (b) Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 3674. (c) Rauk, A.; Alewood, P. F. *Can. J. Chem.* **1977**, *55*, 1498. (d) McLean, A. D.; Loew, G. H.; Berkowitz, D. S. *J. Mol. Spectrosc.* **1977**, *61*, 184. (e) Mavridis, A.; Harrison, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7651. Moderhack, D. *Chimia* (*Switz.*) **1980**, *34*, 449. (f) Wentrup, C.; Gerecht, B.; Laqua, D.; Briehl, H.; Winter, H.-W.; Reisenauer, H. D.; Winnewisser, M. *J. Org. Chem.* **1981**, *46*, 1046. (g) Teles, J. H.; Maier, G.; Hess, B. A., Jr.; Schaad, L. J.; Winnewisser, M.; Winnewisser, B. P. *Chem. Ber.* **1989**, *122*, 753, 1219.

(5) Turner, B. E. *Astrophys. J. Suppl. Ser.* **1989**, *70*, 539–622.

(6) Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *Astrophys. J. Lett.* **1987**, *317*, L 115. Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifer, N.; Suzuki, H.; Ohishi, M. *Astrophys. J. Lett.* **1987**, *317*, L 119.

(7) C_2S_2: Sülzle, D.; Schwarz, H. *Angew. Chem.* **1988**, *100*, 1384; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1337. Maier, G.; Reisenauer, H. P.; Schrot, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1464. Wentrup, C.; Kambouris, P.; Evans, R. A.; Owen, D.; Macfarlane, G.; Chuche, J.; Pommelet, J. C.; Cheikh, A. B.; Plisnier, M.; Flammang, R. *J. Am. Chem. Soc.* **1991**, *113*, 3130. C_2OS: Sülzle, D.; Terlouw, J. K.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 628.

(8) Paton, R. M. *Chem. Soc. Rev.* **1989**, *18*, 33–52.

(9) Powell, F. X. *Chem. Phys. Lett.* **1975**, *33*, 393.

(10) Chivers, T. *Chem. Rev.* **1985**, *85*, 341–365.

(11) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773.

(12) (a) Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1981**, *20*, 1792. (b) Kass, S. R.; DePuy, C. H. *J. Org. Chem.* **1985**, *50*, 2874.

(13) Chivers, T.; Cordes, A. W.; Oakley, R. T.; Swepston, P. N. *Inorg. Chem.* **1981**, *20*, 2376.

(14) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. *Can. J. Chem.* **1984**, *62*, 712.

(15) Golloch, A.; Kuss, M. *Z. Naturforsch.* **1972**, *27B*, 1280.

(16) Herberhold, M.; Ehrenreich, W. *Angew. Chem.* **1982**, *94*, 645; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 633.

(17) Herberhold, M. *Comments Inorg. Chem.* **1988**, *7*, 53–72.

(18) Conti, M.; Trsic, M.; Laidlaw, W. G. *Inorg. Chem.* **1986**, *25*, 254.

(19) Ruppert, I.; Bastian, V.; Appel, R. *Chem. Ber.* **1974**, *107*, 3426. Appel, R.; Ruppert, I.; Milker, R.; Bastian, V. *Chem. Ber.* **1974**, *107*, 380. cf. Weiss, J.; Ruppert, I.; Appel, R. *Z. Anorg. Allgem. Chem.* **1974**, *406*, 329. cf. Chapman, D.; Massey, A. G. *Trans. Faraday Soc.* **1962**, *58*, 1291. Fritz, H. P.; Bruchhaus, R. *Electrochim. Acta* **1984**, *29*, 947.

(20) Jensen, K. A.; Pedersen, C. *Adv. Heterocycl. Chem.* **1964**, *3*, 263–284.

(21) Holm, A. *Adv. Heterocycl. Chem.* **1976**, *20*, 145–174.

(22) Kirmse, W. *Chem. Ber.* **1960**, *93*, 2353.

(23) Lieber, E.; Rao, C. N. R.; Orlowski, R. C. *Can. J. Chem.* **1963**, *41*, 926.

(24) Jensen, K. A.; Holm, A.; Huge-Jensen, E. *Acta Chem. Scand.* **1969**, *23*, 2919.

(25) Jensen, K. A.; Burmester, S.; Bak, T. A. *Acta Chem. Scand.* **1967**, *21*, 2792.

(26) (a) Jensen, K. A.; Holm, A. In *The Chemistry of Cyanates and Their Thio Derivatives*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1977; pp 569–618. (b) Martin, D. *Z. Chem.* **1967**, *7*, 123. Martin, D.; Bacaloglu, R. *Organische Synthesen mit Cyansäureestern*; Academie-Verlag: Berlin, 1980.

(27) Holm, A.; Carlsen, L.; Larsen, E. *J. Org. Chem.* **1978**, *43*, 4816.

(28) Carlsen, L.; Holm, A.; Snyder, J. P.; Koch, E.; Stilkerieg, B. *Tetrahedron* **1977**, *33*, 2231.

(29) Wentrup, C.; Fischer, S.; Maquestiau, A.; Flammang, R. *J. Org. Chem.* **1986**, *51*, 1908.

(30) Bender, H.; Carnovale, F.; Peel, B.; Wentrup, C. *J. Am. Chem. Soc.* **1988**, *110*, 3458.

(31) Brown, R. D.; Elmes, P. S.; McNaughton, D. *J. Mol. Spectrosc.* **1990**, *140*, 390.

(32) Bak, B.; Christiansen, J. J.; Nielsen, O. J.; Svanholt, H. *Acta Chem. Scand.* **1977**, *A31*, 666.

(33) Koch, W.; Frenking, G. *J. Phys. Chem.* **1987**, *91*, 49.

(34) Pyykkö, P. *Chem. Phys. Lett.* **1989**, *162*, 349.

(35) Cole, S. B.; Kleinberg, J. *Inorg. Chim. Acta* **1974**, *10*, 157.

(36) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485.

(37) Kambouris, P.; Plisnier, M.; Flammang, R.; Terlouw, J. K.; Wentrup, C. *Tetrahedron Lett.* **1991**, *32*, 1487.

(38) Franz, J. E.; Black, L. L. *Tetrahedron Lett.* **1970**, 1381.

(39) Senning, A.; Kelly, P. *Acta Chem. Scand.* **1967**, *21*, 1871.

(40) Muhlbauer, E.; Weiss, W. Brit. 1,079,348, Aug. 16, 1967; Ger. Appl. May 8, 1965; *Chem. Abstr.* **1968**, *68*, 69000.

(41) Howe, R. K.; Franz, J. E. *J. Chem. Soc., Chem. Commun.* **1973**, 524.

(42) Howe, R. K.; Gruner, T. A.; Carter, L. G.; Black, L. L.; Franz, J. E. *J. Org. Chem.* **1978**, *43*, 3736.

(43) Brownsort, P. A.; Paton, R. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2339.

(44) Howe, R. K.; Franz, J. E. *J. Org. Chem.* **1978**, *43*, 3742.

(45) McKie, M. C.; Paton, R. M. *J. Chem. Res.* (*S*) **1987**, 245.

(46) Paton, R. M.; Ross, J. F. *J. Chem. Soc., Chem. Commun.* **1980**, 1194.

(47) Brownsort, P. A.; Paton, R. M.; Sutherland, A. G. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1679.

(48) Crosby, J. Ger. Offen. 2,638,029, March, 10, 1977; *Chem. Abstr.* **1977**, *86*, 156824h.

(49) (a) Mortier, R. M.; Paton, R. M.; Scott, G.; Stobie, I. *Brit. Polymer J.* **1987**, *19*, 303. (b) Paton, R. M.; Stobie, I.; Mortier, R. M. *Phosphorus Sulfur* **1983**, *15*, 137. (c) Paton, R. M.; Stobie, I.; Mortier, R. M. *J. Polymer Sci.: Polym. Lett. Ed.* **1983**, *21*, 145.

(50) Howe, R. K.; Franz, J. E. *J. Org. Chem.* **1974**, *39*, 962.

(51) Buttel, D. K.; Simons, B. P.; Deceuninck, J. A.; Hoornaert, G. J. *J. Org. Chem.* **1984**, *49*, 2165.

(52) Howe, R. K.; Franz, J. E. *J. Org. Chem.* **1977**, *42*, 1813.

(53) Howe, R. K.; Shelton, B. R. *J. Org. Chem.* **1981**, *46*, 771.

(54) Greig, D. J.; McPherson, M.; Paton, R. M.; Crosby, J. *Phosphorus Sulfur* **1986**, *26*, 151.

(55) Hogan, I. T.; Sainsbury, M. *Tetrahedron* **1984**, *40*, 681.

(56) Greig, D. J.; Hamilton, D. G.; McPherson, M.; Paton, R. M.; Crosby, J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 607.

(57) Franz, J. E.; Howe, R. K.; Pearl, H. K. *J. Org. Chem.* **1976**, *41*, 620.

(58) Rösch, W.; Regitz, M. *Synthesis* **1987**, 689.

(59) Gould, R. O.; Paton, R. M.; Ross, J. F.; Walkinshaw, M. D.; Crosby, J. *J. Chem. Res.* (*S*) **1986**, 156.

(60) Damas, A. M.; Gould, R. O.; Harding, M. M.; Paton, R. M.; Ross, J. F.; Crosby, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2991.

(61) Wai, K.-F.; Sammes, M. P. *J. Chem. Soc., Chem. Commun.* **1988**, 852.

(62) Beck, W.; Leidl, E.; Kembler, M.; Nagel, U. *Chem. Ber.* **1980**, *113*, 1790.

(63) Sanders, M. J.; Dye, S. L.; Miller, A. G.; Grunwell, J. R. *J. Org. Chem.* **1979**, *44*, 510.

(64) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

(65) Greig, D. J.; Paton, R. M.; Rankin, J. G.; Ross, J. F.; Crosby, J. *Tetrahedron Lett.* **1982**, *23*, 5453.

(66) Holm, A.; Toubro, N. H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1445.

(67) Greig, D. J.; McPherson, M.; Paton, R. M.; Crosby, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1205.

(68) Paton, R. M.; Robertson, F. M.; Ross, J. F.; Crosby, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1517.

(69) Paton, R. M.; Robertson, F. M.; Ross, J. F.; Crosby, J. *J. Chem. Soc., Chem. Commun.* **1980**, 714.

(70) (a) Gotthardt, H. *Tetrahedron Lett.* **1971**, 1277. (b) Gotthardt, H. *Chem. Ber.* **1972**, *105*, 188. (c) Gotthardt, H.; Reiter, F.; Kromer, C. *Liebigs Ann. Chem.* **1981**, 1025.

(71) (a) Gotthardt, H. *Tetrahedron Lett.* **1971**, 1281. (b) Gotthardt, H. *Chem. Ber.* **1972**, *105*, 196.

(72) Rösch, W.; Richter, H.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1809.

(73) (a) Yoshida, H.; Taketani, H.; Ogata, T.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3124. (b) A referee has suggested a Grob fragmentation of **31**, giving diphenyl sulfide, nitrile, and elemental sulfur directly.

(74) (a) Grunwell, J. R.; Dye, S. L. *Tetrahedron Lett.* **1975**, 1739. (b) Sanders, M. J.; Grunwell, J. R. *J. Org. Chem.* **1980**, *45*, 3753.

(75) (a) Bahadir, M.; Nitz, S.; Parlar, H.; Kork, F. *J. Agric. Food Chem.* **1979**, *27*, 815. (b) Machida, M.; Oda, K.; Kanaoka, Y. *Tetrahedron Lett.* **1984**, *25*, 409.

(76) El-Wassiny, M. T. M.; Jørgensen, K. A.; Lawesson, S.-O. *Tetrahedron* **1983**, *39*, 1729.

(77) Takikawa, Y.; Shimada, K.; Sato, K.; Sato, S.; Takizawa, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 995.

(78) Benn, M. *Pure Appl. Chem.* **1977**, *49*, 197–210.

(79) Holm, A.; Harrit, N.; Beckgaard, K.; Buchardt, O.; Harnung, S. E. *J. Chem. Soc., Chem. Commun.* **1972**, 1125.

(80) Holm, A.; Harrit, N.; Toubro, N. H. *Tetrahedron* **1976**, *32*, 2559.

(81) Harrit, N.; Holm, A.; Dunkin, I. R.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1227.

(82) Holm, A.; Harrit, N.; Toubro, N. H. *J. Am. Chem. Soc.* **1975**, *97*, 6197.

(83) Holm, A.; Harrit, N.; Trabjerg, I. *J. Chem. Soc., Perkin Trans. 1* **1978**, 746.

(84) Wentrup, C.; Kambouris, P., to be published.

(85) Maquestiau, A.; Flammang, R.; Plisnier, M.; Wentrup, C.; Kambouris, P.; Paton, R. M.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Proc.* **1990**, *100*, 477.

(86) Kambouris, P.; Plisnier, M.; Flammang, R.; Terlouw, J. K.; Wentrup, C., to be published.

(87) Holm, A.; Christiansen, J. J.; Lohse, C. *J. Chem. Soc., Perkin Trans. 1* **1979**, 960.

(88) Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902.