phosphate complex. We already know that its space group is $P2^1$, $a = 18.016$ (4), $b = 8.622$ (2), and $c = 13.420$ (3) Å.

On another hand, we are checking the use of these chiral crown ethers to separate enantiomers when covalently fixed on silica gel and to induce enantiomeric excess in carbanionic reactions performed by phase-transfer catalysis.

Acknowledgment. We are very indebted to the "Délégation Générale à la Recherche Scientifique" (Grant 79-7-1447) for its financial support.

Dinitrogen Sulfide

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The thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole (**1**) has been the subject of several studies.[2,3] In the most recent investigation,[3] four possible routes, A–D, were considered (Scheme I). Routes A and B were excluded on the grounds that no kinetic isotope effect was observed when the nitrogen atom in position 2 was substituted for ^{15}N. However, the introduction of ^{15}N in position 4 gave rise to a kinetic isotope effect of 1.04, in excellent agreement with a calculated isotope effect 1.041 for N(3)–N(4) bond breaking. However, N_2S was not detectable as a product of the decomposition, and route C was, therefore, excluded. It was concluded[3] that the reaction proceeded via reversible ring opening to thiobenzoyl azide (**2**) (not observed), which then rapidly decomposes to benzonitrile, N_2, and S. On the product side, benzonitrile was formed in virtually 100% yield at temperatures below 100 °C, and in ca. 96% yield together with ca. 4% phenyl isothiocyanate (PhNCS) on gas-phase pyrolysis at 300 °C.[3]

We now wish to report that, contrary to the above conclusion, N_2S is indeed formed as a reactive intermediate in the thermal decomposition of **1**.

1 was subjected to flash vacuum pyrolysis in an apparatus with contact times of ca. 1 ms and permitting the isolation of the products at 77 K or in Ar matrix at 20 K for IR spectroscopic examination. Pyrolyses were carried out at temperatures between 300 and 400 °C. Two prominent products, absorbing at 2228 (benzonitrile) and 2030 cm^{-1}, respectively, were observed. In addition, weak bands at 2175 and 2120 cm^{-1} are ascribed to traces of phenyl isothiocyanate. The IR spectrum resulting from a 400 °C pyrolysis with Ar matrix isolation at 20 K is shown in Figure 1.

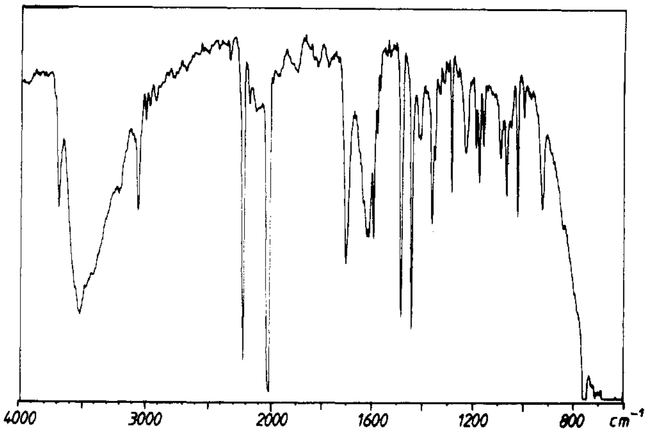

Figure 1. IR spectrum of the products of pyrolysis of 1 at 400 °C (Ar matrix, 20 K).

Scheme I

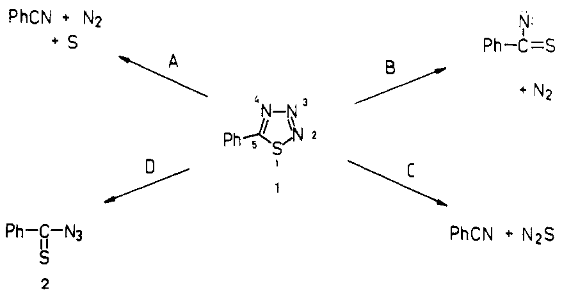

Table I. Infrared, Electronegativity, and Ionization Data for Diazonium Betaines

compd a		compd b	$\bar{\nu}$, cm^{-1} [a]	EN_X [b]	IP, eV[c]
$N{\equiv}N^+C^-H_2$	↔	$N^-{=}N^+{=}CH_2$	2050	2.5	9.0
$N{\equiv}N^+N^-H$	↔	$N^-{=}N^+{=}NH$	2130	3	11.5
$N{\equiv}N^+O^-$	↔	$N^-{=}N^+{=}O$	2224	3.5	12.9
$N{\equiv}N^+S^-$	↔	$N^-{=}N^+{=}S$	2030	2.5	10.4[d]

[a] From IR spectrum. [b] Electronegativity of affixed atom X in N_2X. [c] First ionization potential, experimental values, from ref 7a, unless otherwise stated. [d] MNDO calculated value, from: Sensarma, S., Turner, A. G. *Inorg. Chim. Acta* **1982**, *64*, L 161.

The intensity of the 2030 cm^{-1} band decreased relative to that of benzonitrile as the pyrolysis temperature was increased from 300 to 400 °C and above, thereby indicating that the 2030 cm^{-1} species is unstable and thermally decomposes. Although stable in the solid state at 77 K, this species disappeared on slow warming to 160 K. At the same time, the previously light yellow and transparent solid faded and became opaque, presumably due to the formation of sulfur. After further warming to room temperature, benzonitrile and sulfur were isolable, each in nearly quantitative yield.

An IR spectrum very similar to the one shown in Figure 1 was also obtained on Ar matrix photolysis of 1 at 310 ± 11 nm (2228 (w), 2030 cm^{-1} (m)). Photolysis was very slow at this wavelength. Photolysis was faster with 254-nm light, giving the 2228 and 2230 cm^{-1} bands with equal intensity, and, in addition, very weak bands at 2190 and 2120 cm^{-1} due to phenyl isothiocyanate.

The important 2030 cm^{-1} species cannot be due to benzonitrile sulfide (PhCNS), which we have shown in other work to absorb at 2270 cm^{-1},[4] and in agreement with Holm,[3] no PhCNS is formed in the thermal decomposition of **1**. Thiobenzoyl azide (**2**) is not a good candidate either, since azides generally absorb near 2130 cm^{-1} in the IR, although the thioacyl group may cause a shift toward lower

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[1] (a) University of Queensland. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the University of Queensland. (b) University of Marburg. (c) Université Mons.

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Table II. Mass Spectra of 1 at Various Temperatures (T) and Ionizing Energies (E)[a]

		m/z												
T, °C	E, eV	163	135	103	77	76	64	60	51	50	39	34	32	28
60	70	32	77	80	100	34	15	1	39	26	15	2	5	12
120	70	20	45	100	60	34	8	1	21	16	7	2	2	14
190	70	6	27	100	35	37	10	2	16	17	6	2	4	11
240	70	2	6	100	13	32	3	3	8	13	5	5	3	28
240	70	6	19	23[b]	41	100	9	9	25	41	16	16	9	88
240	14	25	100	93[b]	41	70	27	17			1	66	8	6
240	10	20	100	55[b]	5	18	27	15				47		

[a] Recorded on modified triple sector (E/B/E) MS 902 spectrometer[8] at 8 kV, 200 μA, using direct inlet. [b] m/z 104 given instead of much stronger m/z 103 (benzonitrile) in order to better show spectral differences. Spectra renormalized with respect to second most intense peak.

wavenumbers.[5] **2** should be kinetically unstable, rapidly cyclizing to **1** on warming.[3] However, no trace of **1** could be found after warming the pyrolysates (e.g., the one shown in Figure 1) to room temperature, although as stated above the 2030-cm^{-1} species disappeared at 160 K. We are therefore left with N_2S as the most likely candidate for the 2030-cm^{-1} species.

No clear identification of N_2S has been reported in the literature. Powell[6] identified N_2S as the carrier of a CS_2–N_2 laser and ascribed transitions between 876.9 and 866.2 cm^{-1} to this species. The compound was claimed to be stable at room temperature and unreactive, but no further details were given. However, since nitrile sulfides are known to be unstable and readily eliminate sulfur,[4] the same would be expected of N_2S.

The asymmetric stretching vibrations of the known diazonium betains (CH_2N_2, NH_3, and N_2O) are given in Table I. The changes in the absorption frequency cannot be due solely to the different masses of the affixed groups X in $N{\equiv}N^{+}X^{-}$ but rather to an electronic effect on the force constants. Thus, increasing electronegativity of X is seen to shift the absorption toward higher wavenumbers. This implies that an increased electronegativity of X favors canonical form a of the molecules (see Table I). This is also seen in a frontier molecular orbital treatment of the betaines[7] and leads to lowering of the HOMO energies when going from CH_2N_2 to HN_3 to N_2O (Table I). It is seen that the electronegativity of sulfur is very close to that of carbon, so that an absorption frequency of 2030 cm^{-1} for N_2S is perfectly reasonable. Furthermore, one should expect the chemical reactivity of N_2S to be between those of CH_2N_2 and HN_3. In other words, a comparison between N_2S and the very stable and unreactive N_2O is not relevant.

We conclude that the species absorbing strongly at 2030 cm^{-1} can only be N_2S. In order to prove this, we also obtained the mass spectra of N_2S by pyrolyzing **1** at 100–300 °C directly in the ion source of a modified triple sector mass spectrometer.[8]

The mass spectra are given as a function of temperature in Table II. The molecular ion of **1** (m/z 163) decreases with increasing temperature and, at the same time, the signals at m/z 103 (benzonitrile), 28 (N_2), 32 (S), and 60 (N_2S) increase. A high-resolution mass measurement of m/z 60 gave an exact mass of 59.9779 in excellent agreement with the calculated value for N_2S (59.9782).

A reduction of the ionization potential to 10–14 eV (Table II) caused a simplification of the spectrum, as expected, and the major components are seen to be benzonitrile (m/z 103, 77, 76), N_2S (m/z 60), S_2 (m/z 64; exact mass 63.9420), H_2S (m/z 34), and a molecule with m/z 135, presumably PhNCS which was also observed by IR spectroscopy (vide supra).

Taken together, the IR and MS results demonstrate that benzonitrile and N_2S are significant pyrolysis products; i.e., path C is operating. These results do not exclude the possibility of existence of further routes to benzonitrile, e.g., the concerted path A, or fragmentation via thiobenzoylnitrene (path B), which would rapidly lose sulfur to give PhCN. However, paths A and B were already excluded by Holm.[3] Furthermore, the fact that S_2 appears to be a significant product as judged from the low-voltage mass spectrum (Table II) militates against routes A and B and suggests that N_2S decomposes in a bimolecular process ($2N_2S \rightarrow 2N_2 + S_2$). We reached the same conclusion for nitrile sulfides (RCNS)[4] which are observable after gas-phase formation at 600 °C even though the activation energy for decomposition into RCN and S is reported to be only 4.5 kcal/mol in solution.[9] If this were a unimolecular reaction, nitrile sulfides would not be expected to survive gas-phase pyrolysis.

Experimental Section

Pyrolyses for IR observation were carried out at ca. 10^{-4} torr in a reactor employing a 5 × 0.8 cm (i.d.) quartz tube. The products were collected on KBr or BaF_2 windows mounted on Air Products liquid N_2 cryostats at −196 °C or in Ar matrix at 12–20 K using a Leybold-Heraeus R 210 closed cycle liquid He cryostat. IR spectra were recorded on a Perkin-Elmer 281 IR spectrometer with a working resolution of ca. 2 cm^{-1}. Mass spectra were recorded on a modified triple sector AEI MS 902 mass spectrometer[8] (accelerating voltage 8 kV; electron ionization at 70–10 eV; current 100–500 μA) using a direct insertion probe at various source temperatures. High-resolution mass spectra were run on a Varian 311A instrument.

5-Phenyl-1,2,3,4-thiatriazole[2b] (1) was recrystallized three times from dilute ethanol, dried in vacuum, and had mp 95 °C (lit.[2a] mp 94–95 °C; lit.[2b] mp 95–96 °C): IR (KBr) 3060 (m), 1592 (m), 1578 (w), 1450 (s), 1400 (s), 1360 (w), 1330 (m), 1310 (m), 1287 (w), 1255 (s), 1235 (w), 1200 (m), 1175 (m), 1157 (w), 1090 (w), 1070 (m), 1045 (w), 1020 (s), 998 (w), 905 (m), 755 (s) cm^{-1}.

Pyrolysis of 1 at 300 °C with isolation of the products at −196 °C gave the following IR spectrum: 3060 (w), 2228 (s), 2170 (vw), 2120 (vw), 2030 (m), 1595 (m), 1485 (m), 1450 (m), 1440 (s), 1400 (s), 1365 (w), 1315 (w), 1290 (w), 1260 (m), 1240 (m), 1200 (w), 1190 (w), 1175 (w), 1160 (w), 1090 (w), 1070 (w), 1050 (m), 1020 (m), 1000 (w), 925 (m), 910 (w), 835 (w), 755 (s), 720 (m) 680 (s), 665 (m), 655 (m) cm^{-1}.

This is a composite spectrum of the starting material (**1**), benzonitrile, and N_2S (2030 cm^{-1}).

Pyrolysis of 1 at 400 °C with isolation of the products at −196 °C gave the following IR spectrum: 2330 (w) (CO_2), 2228 (s) (benzonitrile), 2170 (w), 2030 (m), 1595 (m), 1580 (w), 1485 (s), 1440 (s), 1420 (w), 1365 (w), 1290 (m), 1235 (w), 1190 (w), 1175 (w), 1160 (w), 1090 (w), 1070 (m), 1045 (w), 1025 (m), 1000 (w), 925 (m), 750 (s), 680 (s), 665 (s) cm^{-1}.

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The product was light yellow. The 2030-cm^{-1} band and the yellow color disappeared on warming to −110 to −100 °C and the sample became opaque. Benzonitrile and sulfur were identified after warming to room temperature.

Pyrolysis of 1 at 400 °C with isolation of the products in Ar matrix on a BaF_2 window at 20 K was carried out at ca. 10^{-5} torr at an argon/substance ratio of 500:1. The IR spectrum (Figure 1) had the following bands: 3060 (m), 2228 (s), 2175 (vw), 2125 (vw), 2030 (s), 1700 (acetone), 1620 (water), 1595 (m), 1485 (m), 1440 (m), 1408 (w), 1360 (m), 1285 (w), 1230 (w), 1190 (w), 1175 (w), 1155 (w), 1090 (w), 1065 (w), 1020 (w), 995 (vw), 920 (m), 750 (s) cm^{-1}.

No 1 was present in this spectrum, and no 1 was detectable after warming this sample to room temperature. Benzonitrile, sulfur, and a trace of phenyl isothiocyanate were the only products still detectable at room temperature.

Photolysis of 1 in Ar matrix at 11 K at 310 ± 11 nm (Hanovia 1000-W high-pressure Hg lamp with Schoeffel GM 250 monochromator) for 2 h caused the appearance of a weak band at 2030 cm^{-1} and a still weaker one at 2228 cm^{-1}.

Irradiation at 254 nm (75-W low-pressure Hg lamp) for 3 h caused the appearance of two equally strong bands at 2030 and 2228 cm^{-1} together with very weak absorptions at 2190 and 2120 cm^{-1}, the latter ascribed to phenyl isothiocyanate.

Registry No. 1, 34733-85-2; N_2S, 56400-02-3; PhNCS, 103-72-0; PhCN, 100-47-0.

Reactions of 4,5-Dihydro-2-thiazolamine with Phenyl Isothiocyanate and Phenyl Isocyanate: A Reinvestigation

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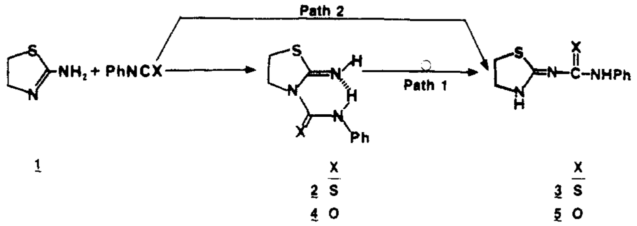
In 1928, Fromm and Kapeller-Adler reported the reaction of 4,5-dihydro-2-thiazolamine (1) with phenyl isothiocyanate under "starker Kühlung" conditions, which initially produced the unstable 2-imino-*N*-phenyl-3-thiazolidinecarbothioamide (2).[1] Fromm et al. hypothesized that 2 rearranged during the heating process to *N*-phenyl-*N*′-2-thiazolidinylidenethiourea (3), which melted at a higher temperature. Klayman, Maul, and Milne were unable to repeat the earlier work after "careful repetition" of Fromm's conditions.[2,3] Instead, Klayman et al. obtained a single product to which structure 2 was assigned based on an "unequivocal" synthesis.[2] Later, Klayman retracted structure 2, along with its alleged synthesis, then reassigned structure 3 to this product,[3] which later was confirmed by X-ray crystallography.[4] The X-ray data could not distinguish the tautomeric composition of 3 because both C$\overset{\cdots}{-}$N bond lengths were similar. However, Klayman et al. stated that "the intermediacy of 2 in the formation of 3 could not be precluded."[3]

Klayman, Maul, and Milne also examined the reaction of 1 with phenyl isocyanate in acetonitrile in an attempt to prepare 2-imino-*N*-phenyl-3-thiazolidinecarboxamide (4).[2] The only product isolated was *N*-phenyl-*N*′-2-thiazolidinylideneurea (5) whose structure was deduced by ^{15}N-labeling and degradation experiments. Klayman et al. concluded that phenyl isocyanate had reacted *only* with the exocyclic amino group of 1.[2]

Scheme I



a. X = S, 1·HBr, KOH/EtOH, −4 to −2 °C.
b. X = S, 1, Et_2O, −7 to −5 °C.
c. X = O, 1, Et_2O, −16 to −12 °C.

In our hands, reaction of 1 with phenyl isothiocyanate (Scheme Ia) resulted in almost exclusive formation of thiocarbanilide 2, when compared on TLC with an authentic sample of thiourea 3.[3] A small amount of 3 was observed in the crude product. Recrystallization in the cold furnished pure 2 in 51% yield,[5,6] the TLC of which indicated some dissociation to 1 and phenyl isothiocyanate (verified by two-dimensional TLC). We also prepared carbothioamide 2 under more convenient Scheme Ib, conditions, which provided pure 2 in 53% yield. Scheme Ia,b conditions appear to show incomplete reaction of 1 with phenyl isothiocyanate, even in the presence of excess (10–20%) 1 during reaction times of up to 3 h. These observations are consistent with the reversible dissociation of pure 2 to 1 and PhNCS in solution and, probably, also during fusion of neat 2. As a result, during experiments in which 2, neat or in solution, is heated causing conversion to 3, the presence of PhNCS allows formation of varying amounts of a byproduct derived from cyclization of a bis adduct of 1 with phenyl isothiocyanate, as previously reported by Klayman et al.[7] Thiocarbanilide 2 was also unstable in the solid state at −20 °C since the presence of 3 was detected after 1 month.

Reaction of 1 with an equimolar quantity of phenyl isocyanate at 0–5 °C in acetonitrile gave 4 as the major product along with small amounts of 1, 5, and a bis adduct.[3] At ambient temperature, 5 became the major product (ca. 67% by ^1H NMR). However, when phenyl isocyanate was allowed to react with a 10% excess of 1 under Scheme Ic conditions, a 73% yield of pure carboxanilide 4 was obtained directly from the reaction mixture. Amide 4 was significantly more stable than thio counterpart 2 in the solid state and in solution (vide infra). Conversion of 4 to 5 was essentially quantitative when heated neat or in solution. The structure of 4 (and 2 by analogy) has been verified by X-ray crystallography.[8]

^1H NMR spectra of 2 were obtainable by dissolution in CD_2Cl_2 in the cold and immediately recording the spectra at −50 °C probe temperature. In DMF-d_7, dissociation of 2 to 1 and phenyl isothiocyanate was so rapid at −30 °C that clean spectra could not be obtained. ^{13}C NMR verified the presence of PhNCS and ^1H NMR showed varying amounts (ca. 1–2 H) of resonances ascribable to the 4,5-protons of 1. In contrast, carboxanilide 4 was significantly

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(5) We were generally unable to observe spontaneous crystallization after 2 melted. Crystallization of the melt was induced by scratching with a slender glass boiling stick.

(6) The mps of 2–5 were variable (ca. ±2 °C) with the rate of heating.

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