Rieveschl, Jr., and F. E. Ray, *Chem. Rev.*, **23**, 287 (1938).
(17) C. Courtot and R. Geoffroy, *C. R. Held Seances Acad. Sci.*, **178**, 2259 (1924).
(18) A. Mathieu, *Bull. Soc. Chim. Fr.*, 1533 (1971).
(19) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **92**, 1605 (1970).
(20) B. W. Erickson and R. B. Merrifield, *Proteins, 3rd Ed.*, **2**, 255–527 (1976).
(21) B. F. Gisin, *Anal. Chim. Acta*, **58**, 248 (1972).
(22) A. R. Mitchell and R. B. Merrifield, *J. Org. Chem.*, **41**, 2015 (1976).
(23) R. B. Merrifield, A. R. Mitchell, and J. E. Clarke, *J. Org. Chem.*, **39**, 660 (1974).
(24) A. R. Mitchell, B. W. Erickson, M. N. Ryabtsev, R. S. Hodges, and R. B. Merrifield, *J. Am. Chem. Soc.*, **98**, 7357 (1976).
(25) A. R. Mitchell, S. B. H. Kent, B. W. Erickson, and R. B. Merrifield, *Tetrahedron Lett.*, 3795 (1976).
(26) This peptide-resin was prepared by Mark Riemen.
(27) R. B. Merrifield, *Adv. Enzymol.* **32**, 221 (1969).
(28) B. F. Gisin, *Helv. Chim. Acta*, **56**, 1476 (1973).

Thermal Decomposition of 1,2,3,4-Thiatriazoles. On the Question of Thioacyl Azide and Thioacylnitrene Intermediates

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Received December 20, 1977

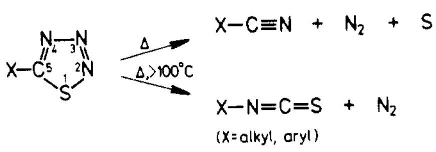
The kinetics of decomposition of 5-phenyl-1,2,3,4-thiatriazole to benzonitrile, sulfur, and nitrogen were investigated in bromobenzene at 52.2–61.1 °C and found to be first order with E_a = 118.0 kJ·mol^{-1} and $\Delta S^{\ddagger}$ = 11.7 J·mol^{-1} K^{-1}. A linear Hammett correlation was obtained with substituted phenylthiatriazoles ($\rho \approx 0$). Kinetic isotope effects with 4-^{15}N- and 2-^{15}N-labeled phenylthiatriazole were observed to be ~4 and 0%, respectively. The effect of Lewis acids and of dipolarophiles on the decomposition was investigated. The overall observations are interpreted to imply a three-step mechanism via (*E*)-thiobenzoyl azide. There is no evidence for a thiobenzoylnitrene intermediate. Phenyl isothiocyanate, which is formed from phenylthiatriazole above ~100 °C, is suggested to result from a concerted rearrangement from (*Z*)-thiobenzoyl azide.

Thiatriazoles (5-substituted 1,2,3,4-thiatriazoles) decompose at room temperature or on slight heating, giving rise to sulfur, nitrogen, and an organic compound, generally in high yields (Scheme I).[1] Alkyl isothiocyanates are reported to be formed when the decomposition of alkylthiatriazoles is carried out at elevated temperature (Scheme I), while at room temperature only alkanenitriles are formed.[2] The thermal decomposition of thiatriazoles has attracted attention because of the synthetic possibilities of this reaction[1] and because of the possible intermediacy of hitherto unknown types of compounds: thioacylnitrenes, RC(=S)N̈:; thiazirines, $\overline{\text{RC=NS}}$; and thioacyl azides, R(C=S)N_3.[3]

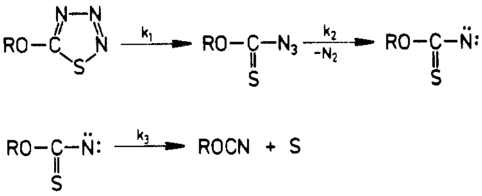
Jensen and Holm investigated the thermal decomposition of 2-^{15}N-labeled 5-isobutoxy-1,2,3,4-thiatriazole and found that the nitrogen lost belonged almost exclusively (98.9%) to the N(2) and N(3) positions.[4] No specific conclusions about the existence of intermediates can be drawn from this result.[4]

Jensen et al. studied the kinetics of the thermal decomposition of 5-alkoxy-1,2,3,4-thiatriazoles in dibutyl phthalate at 15–40 °C by manometric measurement of the nitrogen evolved.[5] The reaction was found to be first order with activation energies for different 5-alkoxythiatriazoles of 101.7–104.2 kJ·mol^{-1} and activation entropies of 13.4–19.7 J·mol^{-1} K^{-1}. It was pointed out that the activation energies for the different alkoxythiatriazoles differ very little, in agreement with the assumption that the reaction proceeds via the same mechanism in all cases (Scheme II). The decomposition of 5-alkoxythiatriazoles was compared with the thermal decomposition of alkylthiatriazoles mentioned[2] (Scheme I), and it was assumed that the formation of isothiocyanates in the latter case may be interpreted to mean that thioacylnitrenes, RC(=S)N̈:, are intermediates. These were believed to either lose sulfur and form nitrile or rearrange to isothiocyanate. An analogous byproduct, RO–NCS, was not observed in the thermal degradation of alkoxythiatriazoles.

Scheme I



Scheme II



A scheme was suggested for the decomposition of alkoxythiatriazoles involving opening of the ring with formation of a thioacyl azide as the first step (Scheme II).[5]

Jensen et al. state that if this mechanism is correct, the thioacyl azide must decompose rapidly because the characteristic azide band at approximately 2130 cm^{-1} is not observed in the infrared spectrum of a decomposing thiatriazole.

Pilgram et al.[6] tried to intercept the suggested thioacyl azide intermediate with trivalent phosphorus. With phosphorus triamides, 1:1 reaction products are formed, formulated as 2,2-dihydro-1,3,4,5,2-thiatriazaphosphorines. However, it does not seem possible to decide whether these compounds are formed by attack of the reagent directly on the heterocyclic ring or by attack on a preformed thioacyl azide.

thiobenzoyl chloride and tetrabutylammonium azide were

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Table I. Rate of Decomposition of 5-Phenyl-1,2,3,4-thiatriazole in Bromobenzene at 61.1 °C

k_1, 10^{-5} s^{-1}	$t_{1/2}$, h	log A, s^{-1}	E_a, kJ · mol^{-1}	$\Delta S^{\ddagger}$, J·mol^{-1}·K^{-1}
2.76 ± 0.02	6.97 ± 0.05	13.89 ± 0.52	118.0 ± 4.6	11.7 ± 10.0

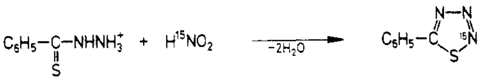
The present investigations were undertaken in the hope of elucidating the question of intermediates in the thermal degradation of thiatriazoles.

Results

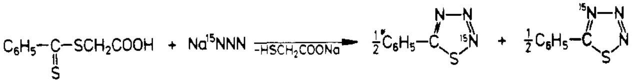
Kinetic Measurements. Thiobenzoyl Azide Trapping Experiments. The kinetics of the decomposition of 5-phenyl-1,2,3,4-thiatriazole were investigated in bromobenzene by electronic absorption spectroscopy. A first-order reaction was observed in agreement with the results of Jensen et al.[5] on 5-alkoxy-1,2,3,4-thiatriazoles. Rate constants were determined in the temperature range 52.2–61.1 °C and were used to calculate the activation parameters (Table I).

Rate constants for substituted phenylthiatriazoles were obtained by the same method as for phenylthiatriazole. A Hammett plot of log (k_{ArX}/k_{ArH}) (X = 4-CH_3O, 4-CH_3, H, 4-Cl, 3-Cl, and 3-NO_2) against σ values gives linear correlations with $\rho = -0.1 \pm 0.05$ (45.0 °C) and 0.2 ± 0.05 (61.1 °C) (Figure 1).

Isotope effects on the decomposition of phenylthiatriazole were studied by means of mass spectrometry. 2-^{15}N- and 4-^{15}N-labeled 5-phenyl-1,2,3,4-thiatriazoles were prepared by previously described procedures[7] (eq 1 and 2) and partially decomposed by heating in benzene. The thiatriazole remaining was determined and decomposed quantitatively by heating to 110 °C for 1 h in an evacuated ampule. The nitrogen gas that formed was analyzed for the ratio between m/e 29 and 28 before and after decomposition to look for a possible kinetic isotope effect.[8] The results shown in Table II reveal the lack of a significant isotope effect in [2-^{15}N]phenylthiatriazole, whereas an increase in the amount of heavier isotope is clearly observed when ^{15}N is introduced into position 4 (Table III). A limiting value of around 1.04 can be estimated from the figures in Table III.



(Eqn. 1)



(Eqn. 2)

Experiments were conducted to trap the suggested thioacyl azide (compare with Scheme II). 5-Phenylthiatriazole was decomposed in aqueous ethanol in the presence of $Na^{15}N_3$ (95% isotopically labeled on one nitrogen) on the assumption that an isotope exchange in the eventually formed thioacyl azide might take place on attack by the nucleophilic azide ion. After approximately 50% of the original thiatriazole had decomposed, that which remained was recovered and submitted to mass spectrometry. The analysis showed that only the natural abundance of ^{15}N was present in the thiatrizole. For comparison, benzoyl azide was treated with $Na^{15}N_3$. Under the prevailing conditions, benzoyl azide gradually decomposed to phenyl isocyanate, which reacted with the water present to form N,N'-diphenylurea. Mass spectral analysis showed that ^{15}N had been incorporated to the extent of 30%, so exchange between benzoyl azide and $^{15}N_3^-$ had taken place (Scheme III). Despite this negative evidence for a thioacyl azide, it was found in another experiment that sodium azide was formed upon decomposition of 5-phenylthiatriazole in the presence of sodium hydroxide. The sodium azide that formed was identified by its reaction with carboxymethyl dithiobenzoate to give 5-phenylthiatriazole in 4% yield (eq 3) based on the starting thiatriazole, according to the general method for the preparation of 5-phenylthiatriazole.[9a]

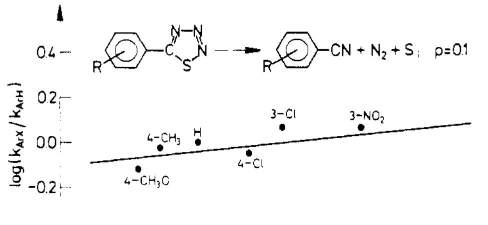
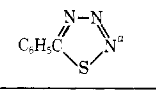


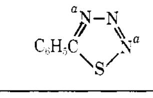
Figure 1. Plot of log (k_{ArX}/k_{ArH}) against σ values (45.0 °C).

Table II. Nitrogen from the Pyrolysis of [2-^{15}N]-Phenylthiatriazole Decomposed to Various Degrees

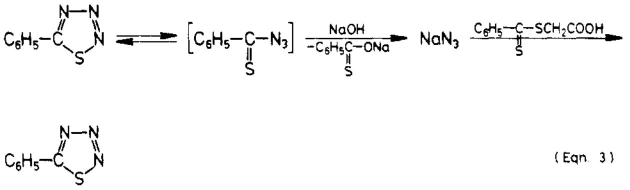
	measd ratio between m/e 29 and m/e 28	cor m/e 29/m/e 28 for contribution from background and air	
initial compound	0.902 ± 0.001 0.901 ± 0.002	0.908 0.905	0.907[b]
73% decomposed at 39–40 °C	0.902 ± 0.002 0.893 ± 0.002	0.906 0.907	0.907[b]
77% decomposed at 80 °C	0.894 ± 0.003 0.892 ± 0.001	0.905 0.899	0.902[b]

[a] Labeled with ^{15}N in about half of the molecules. [b] Mean value.

Table III. Nitrogen from the Pyrolysis of [2- and 4-^{15}N]-Phenylthiatriazole Decomposed to Various Degrees

	measd ratio between m/e 29 and m/e 28	cor m/e 29/m/e 28 for contribution from background and air	
initial compound	0.889 ± 0.001 0.893 ± 0.001 0.892 ± 0.001	0.896 0.900 0.902	0.899[b]
46% decomposed at 39–40 °C	0.874 ± 0.001	0.881	0.881[b]
59% decomposed at 80 °C	0.874 ± 0.001 0.879 ± 0.001	0.881 0.884	0.883[b]
77% decomposed at 80 °C	0.865 ± 0.001 0.868 ± 0.001	0.873 0.873	0.873[b]

[a] Labeled with ^{15}N either in position 2 (47.5%) or in position 4 (47.5%). [b] Mean value.



(Eqn. 3)

Attempts were made to obtain independent information about the unknown thiobenzoyl azide. Ethanolic solutions of

Scheme III

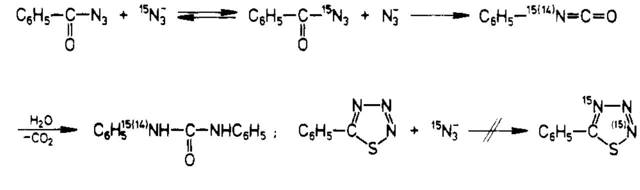


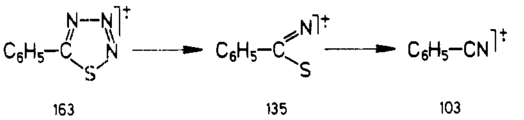
Table IV. Yield of Benzonitrile on Thermal Decomposition of 5-Phenylthiatriazole in the Presence of Various Dipolarophiles

dipolarophile	% benzonitrile	registry no.
MeOOCC≡CCOOMe	100	762-42-5
trans NCCH=CHCN	100	764-42-1
cis EtOOCCH=CHCOOEt	99	141-05-9
$(CN)_2C=C(CN)_2$	91	670-54-2
tetrachloroquinone	97	118-75-2
tetrachloroquinone	92	

thiobenzoyl chloride and tetrabutylammonium azide were mixed at −115 °C, and the reaction was monitored by electronic absorption spectroscopy. Careful warming caused the disappearance of the absorptions due to thiobenzoyl chloride (λ_{max} 526 and 315 nm), which were replaced by the absorption due to phenylthiatriazole (λ_{max} 280 nm), but no transients due to a thiocarbonyl chromophore[10] were observed. Thus, the bimolecular formation of thiobenzoyl azide is succeeded by a more rapid ring closure to thiatriazole.[9b]

Trapping Experiments and Search for Intermediates by Gas Phase Decomposition of Thiatriazoles. Phenylthiatriazole was decomposed in the presence of various dipolarophiles, and the amount of benzonitrile that formed was estimated by means of GLC from calibration curves with electronic integration. As shown in Table IV, a high yield of benzonitrile was obtained in all cases, indicating a lack of reactive transients such as nitrenes (Scheme II).

The possible existence of intermediates was also investigated by means of mass spectrometry. Samples were introduced into the mass spectrometer (pressure = 10^{-5}–10^{-6} torr) by the direct inlet system with the probe temperature kept at 10–20 °C, and decomposition was induced by keeping the ion source at elevated temperatures. The products thus formed were analyzed by electron impact (EI) and field ionization (FI). Jensen et al.[11] and Zeller et al.[12] previously scrutinized the EI spectrum of phenylthiatriazole, which is characterized by the following fragmentations:



The possibility that part of the *m/e* 135 ion might be due to thermal decomposition of nonionized thiatriazole to molecules with mass 135 such as thiobenzoylnitrene or phenyl isothiocyanate was not considered.

The EI and FI mass spectra of phenylthiatriazole (Figure 2) were measured in immediate succession and under the same thermal conditions (ion source at 100 °C and probe at 25 °C). Since field ionization takes place with no energy input (excluding polarization by the high electric field) to the neutral molecule,[13] the EI and FI spectra complement each other well. Whereas EI yields many characteristic fragment ions, FI (even of very unstable substances) gives relatively intense molecular ions and only a few fragment ions.[14] Thus, in the case of phenylthiatriazole the FI spectrum confirms that the two peaks in the EI spectrum at *m/e* 103 and 135 are mainly electron impact induced fragment ions and not thermal decomposition products. The FI spectra of pure benzonitrile and phenyl isothiocyanate show intense molecular ions. Moreover, in the FI spectrum of phenyl isothiocyanate the intensity of the peak at *m/e* 103 was less than 1% of the intensity of the molecular ion. On introducing different mixtures (1:2, 1:1, and 2:1) of phenyl isothiocyanate and benzonitrile into the gas inlet system (kept at 150 °C) of the mass spectrometer, the relative FI weight sensitivity toward the two compounds was found to be phenyl isothiocyanate/benzonitrile = 0.49.

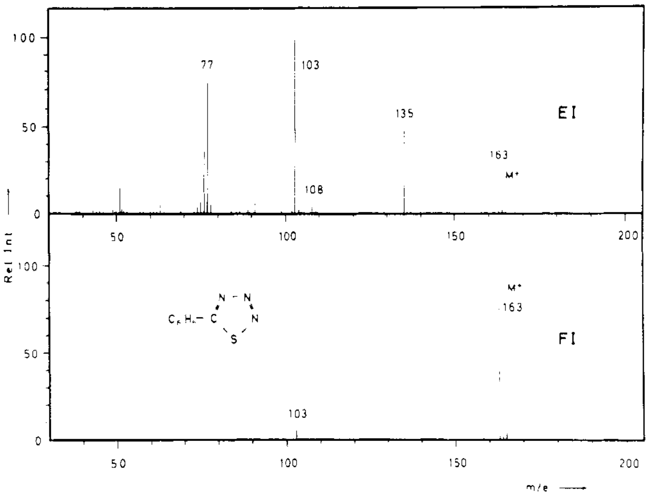


Figure 2. EI and FI mass spectra of phenylthiatriazole.

A typical result of varying the ion source temperature, keeping the probe temperature constant, is shown in Table V. The EI and FI spectra show that the *m/e* 135/*m/e* 163 ratio increases with the temperature. In the case of FI, the ion at *m/e* 135 indicates its thermal formation directly from nonionized thiatriazole. On comparing the ratios *m/e* 135/*m/e* 163 and *m/e* 103/*m/e* 163 in the FI measurements, the weight ratio at about 270 °C between phenyl isothiocyanate and benzonitrile corresponds to ca. 0.06.

It is to be expected that a decrease in the ionizing electron energy results in less fragmentation of the molecular ion. In the present case, on lowering the electron energy and keeping the ion source at 270 °C to ensure thermal decomposition of the phenylthiatriazole the ratio between the ion at *m/e* 135 and the molecular ion at *m/e* 163 decreases until about the appearance potential (AP) of phenylthiatriazole. Then it begins to increase, indicating that, besides the fragment ion at *m/e* 135, there is another ion with mass *m/e* 135 and with an AP lower than that of phenylthiatriazole. AP measurements of the molecular ions of phenylthiatriazole (*m/e* 163) and of phenyl isothiocyanate (*m/e* 135) show that the peak at *m/e* 135 has an AP value that is about 0.3 eV lower than that of the peak at *m/e* 163. We conclude that the above two experiments demonstrate a thermal process from nonionized phenylthiatriazole, M − N_2.

Vapors of phenylthiatriazole (pressure = 0.1 torr) were

Table V. Relative Ion Intensity in the Mass Spectra of 5-Phenylthiatriazole Measured by Electron Impact (EI, 70 eV) and Field Ionization (FI) at Various Ion Source Temperatures[a]

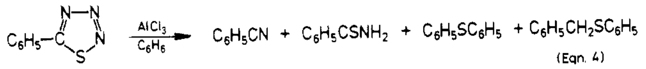
	ion source temp, °C									
	100	130	160	200	245	270	230	180	140	100
m/e EI: 135/163	1.73	1.94	2.37	3.06	3.31	3.60	3.31	3.48	3.21	1.60
m/e EI: 103/163	2.82	4.39	6.2	6.9	13	17	10	8.0	5.8	4.2
m/e FI: 135/163	0.004	0.005	0.003	0.012	0.033	0.036	0.016	0.011	0.007	0.004
m/e FI: 103/163	0.042	0.097	0.088	0.22	0.91	1.27	0.79	0.33	0.15	0.047

[a] Sample temperature, 10–20 °C.

passed through a quartz tube heated to 300 °C, and the products that formed were analyzed by combined GLC–mass spectrometry. The formation of benzonitrile and phenyl isothiocyanate in 95.5–96.2 and 4.5–3.8% yields agrees well with the mass spectrometric finding of ca. 6% isothiocyanate (Table V, 270 °C) and with the appearance potential measurements. Thus, there is no evidence for transient formation of thiobenzoylnitrene.

A search was also made for dinitrogen sulfide, N_2S, in the various spectra, but it was not observed. From the geometry of the ion source and the internal gas pressure, it can be estimated that it takes approximately 10^{-4}–10^{-5} s from the time a molecule decomposes on the walls of the ion source until ionization. Detection of gas phase transients is therefore limited to compounds with lifetimes greater than 10^{-4}–10^{-5} s.

Catalytic Effects on the Decomposition of Thiatriazoles. Jensen et al. studied the decomposition of 5-ethoxythiatriazole in dibutyl phthalate in the presence of various catalysts, including anhydrous aluminum chloride, but practically no effect on the reaction rate was observed.[5] However, the decomposition can indeed be enhanced catalytically by Lewis acids under conditions where the catalyst is not sequestered by complex formation with the solvent. Thus, the addition of aluminum chloride to 5-phenylthiatriazole in benzene causes a brisk evolution of nitrogen at room temperature. When esters or ethers are used as solvents, complexes are formed between the solvent and the catalyst and catalytic rate enhancement is no longer observed, which explains the negative result of Jensen et al. Other Lewis acids such as BF_3, $FeCl_3$, and $GaBr_3$ also catalyze the decomposition. The reaction with $AlCl_3$ in benzene was studied in the hope of obtaining a complex with the unknown thioacyl azide or thioacylnitrene. However, the reaction products are a complex mixture including benzonitrile, thiobenzamide (1.2%), and approximately 10% of diphenyl sulfide, phenyl benzyl sulfide, and other products, proving that this reaction proceeds in a completely different manner from the uncatalyzed reaction of thiatriazole (eq 4).



(Eqn. 4)

In contrast, $TiCl_4$ does not catalyze decomposition, but forms a thermally stable orange 1:1 complex with 5-phenylthiatriazole (eq 5). The characteristic azide band at around 2100 cm^{-1} is absent in the infrared spectrum of the complex. It is sensitive to moisture and is hydrolyzed to the starting thiatriazole on addition of water. After irradiation ($\lambda > 390$ nm) for 18 h, the thiatriazole can be recovered almost unchanged.

(Eqn. 5)

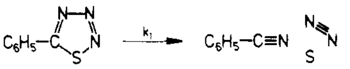
The sulfur extruded in the uncatalyzed reaction is probably primarily eliminated as atoms. In an attempt to determine whether this is able to react with undecomposed thiatriazole, 5-ethoxythiatriazole was added in various concentrations (1–5 equiv) to solutions of 5-phenylthiatriazole in ether. Within the limits of error, 5-phenylthiatriazole could be recovered unchanged while 5-ethoxythiatriazole underwent complete degradation.

Discussion

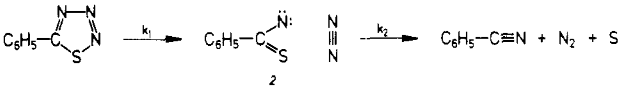
5-Phenylthiatriazoles decompose in first-order reactions, as found for 5-alkoxythiatriazoles by Jensen et al.,[5] and the activation entropy of 11.7 ± 10.0 $J\cdot mol^{-1}\cdot K^{-1}$ is close to that determined for 5-alkoxythiatriazoles (13.4–19.7 $J\cdot mol^{-1}\cdot K^{-1}$).[5] We have no evidence for the operation of different mechanisms in the two cases. The Hammett ρ value around 0 is in agreement with a nonpolar reaction, which may be formed by several discrete steps (eq 9) in which the individual ρ values cancel each other out. The decomposition is catalytically enhanced by Lewis acids, but the catalyzed reaction takes a completely different course and therefore does not provide mechanistic information about the uncatalyzed reaction. Otherwise, the rate of decomposition of thiatriazoles in dibutyl phthalate is not influenced by the addition of acids, bases, or other compounds, which again points to a nonpolar reaction.[5] The almost quantitative yield of benzonitrile from decomposing phenylthiatriazole in various substrates (Table IV) does not point to a radical reaction and excludes possible intermediacy of benzonitrile sulfide (via the thiazirine[3]). Thus dimethyl acetylenedicarboxylate is an efficient trapping agent for nitrile sulfides.[3]

The sulfur extruded in these reactions is probably primarily eliminated as atoms and reacts as "active sulfur". Thus, the addition of triphenylarsine to decomposing 5-ethoxythiatriazole gives rise to triphenylarsine sulfide, which cannot be prepared directly from triphenylarsine and sulfur.[15] The thermally generated sulfur is, however, not sufficiently reactive to react with C–H or C=C bonds.[16] It seemed possible that the atomic sulfur primarily generated might attack undecomposed thiatriazole with formation of S_2, but 5-phenylthiatriazole remains unchanged in the presence of rapidly decomposing 5-ethoxythiatriazole. This observation seems to exclude reaction between thiatriazole and sulfur provided, of course, that atomic sulfur is similarly reactive toward both thiatriazoles.

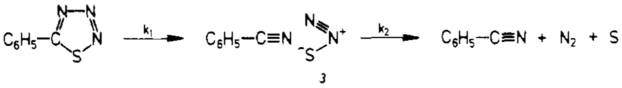
Accordingly, the uncatalyzed decomposition of thiatriazoles may take place in a one-step concerted reaction or via discrete steps, as shown in eq 6–9. Equation 7 may also represent the formation of a three-membered ring (thiazirine).



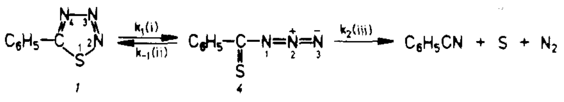
(Eqn. 6)



(Eqn. 7)



(Eqn. 8)



(Eqn. 9)

The first two processes are ruled out because of the lack of a kinetic isotope effect when ^{15}N is introduced into position 2 (Table II) since it is to be expected that direct loss of nitrogen will involve substantial bond breaking between S(1) and N(2) in the transition state. The expected isotope effects for breaking of the S(1)–N(2) and N(3)–N(4) bonds in thiatriazole are calculated to 1.048 and 1.041, respectively, from the force constants estimated for the corresponding bonds in 1,2,5- and 1,3,4-thiadiazole.[17]

The kinetic isotope effect observed ($\approx$ 1.04) upon the introduction of ^{15}N into position 4 (Table III) is a priori in agreement with retrocycloaddition of N_2S (3) (estimated to be 1.041, see above) followed by rapid decomposition to elemental sulfur and nitrogen. However, N_2S has recently been reported to be indentified as carrier in a N_2–CS_2 laser and stable at room temperature.[18] In the present case, all attempts to show the presence of N_2S by mass spectrometry in gas phase decompositions failed, and its lifetime, if it is formed, could be estimated to be at most 10^{-4}–10^{-5} s at 100 °C and above. On this basis we must exclude decomposition via N_2S, and hence only the process in eq 9 is left for discussion.

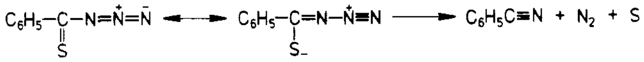
It must be recognized that the first step (i) in eq 9 is reversible (ii); thioacyl azides (**4**) must be intermediates when thiatriazoles are formed from carboxymethyl dithiobenzoate or thiobenzoyl chloride and azide ion. Attempts to trap thiobenzoyl azide in the reaction between thiobenzoyl chloride and azide ion at −110 °C have failed, which points to a very rapid ring closure and suggests that the concentration of thiobenzoyl azide in a thiatriazole decomposition is very small. This is in accordance with the observations of Jensen et al. that the characteristic azide band is not observed in a decomposing thiatriazole.[5] We can therefore treat the decomposition reaction by the steady state approximation,[19] which leads to the following expression:

$$\text{rate} = [\text{thiatriazole}]\frac{k_1 \cdot k_2}{k_{-1} + k_2}$$

This result is clearly in agreement with the observed first-order kinetics, but the activation parameters cannot be evaluated as they are the result of three different reactions (i, ii, and iii). The Hammet ρ value around 0 is similarly the result of the three discrete steps in which the individual ρ values cancel each other.

In the equilibrium between thiatriazole and thiobenzoyl azide (eq 9), both reactions i and ii will be subject to an isotope effect due to the lowering of the zero point energy upon introduction of ^{15}N in position 2 or 4 in the thiatriazole. However, we expect the isotope effects to be of the same magnitude, giving rise to only a small overall isotope effect. By use of the steady state equation ($k_{-1} \gg k_2$; see discussion above), we therefore estimate that the isotope effect observed (≈ 1.04 with ^{15}N in position 4 in the thiatriazole ring, Table III) is mainly the result of bond breaking in thiobenzoyl azide (iii) between N(1) and N(2) (for numbering, see eq 9). For comparison, isotope effects for breaking of the corresponding bonds in phenyl azide and benzoyl azide are calculated and observed to be 1.053 and 1.037, respectively.[20]

Some kinetic isotope effect with ^{15}N in position 3 in thiobenzoyl azide (formed by ring opening of 2-^{15}N-labeled thiatriazole) might be expected because a new bond between N(2) and N(3) is formed. However, as mentioned below, the overall reaction is strongly exoenergetic and, according to the Hammond principle,[21] the transition state will be reactant-like. A significant contribution to a ground state zwitterionic resonance form, as depicted in eq 10, may be responsible for a small kinetic isotope effect in accordance with the experimental results.[22]



$$C_6H_5{-}\underset{\underset{S}{\parallel}}{C}{-}N{=}\overset{+}{N}{=}\overset{-}{N} \longleftrightarrow C_6H_5{-}\underset{\underset{S_-}{|}}{C}{=}N{-}\overset{+}{N}{\equiv}N \longrightarrow C_6H_5C{\equiv}N + N_2 + S$$

(Eqn. 10)

The formation of sodium azide in 4% yield on thermal decomposition of phenylthiatriazole in the presence of sodium hydroxide (eq 3) is clearly in agreement with the suggested reaction sequence (eq 9), although this result alone is hardly definitive evidence.

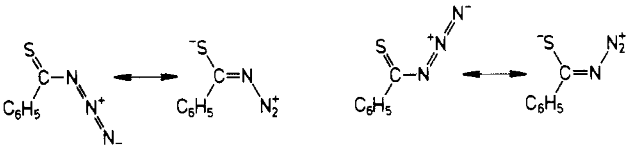
These results are supported by CNDO potential surface calculations on thiatriazole, which suggest that the ring closure is thermally "allowed" with an energy barrier of 63 kJ·mol^{-1}. The ring is calculated to be more stable by 54 kJ·mol^{-1}, and consequently the activation energy for the ring opening is estimated to be 117 kJ·mol^{-1}.[23] Furthermore, CNDO calculations indicate that thiatriazole is only partially delocalized and that the 1,2 bond is essentially a single bond,[23] which may be reflected in the thermochemical properties.

Finally, differential thermal analysis[24] is an agreement with first-order kinetics. A single peak corresponding to an exothermic reaction ($\Delta H \simeq -272$ kJ·mol^{-1}) is observed in the thermogram, but the mechanistic coordinates[25] exhibit small deviations from the theoretical values derived for a pure first-order reaction[26] ($S_{\text{found}} = 0.39$–0.46, $S_{\text{theor.}} = 0.55$; $M_{\text{found}} = 0.0050$–$0.0045$, $M_{\text{theor.}} = 0.0047$), which is not in disagreement with eq 9. The appearance of only one peak in the thermogram may be explained by k_{-1} and $k_2 \gg k_1$.[27]

There is no evidence for an intermediate thioacylnitrene (**2**) in these reactions, and loss of sulfur from the thioacyl azide has therefore tentatively been depicted as a concerted process. The general concept of a typical nitrene is a high energy, hyperreactive species, electrophilic and radical-like in its triplet ground state,[28] but we cannot exclude that the properties of a thioacylnitrene may be unusual with a very short lifetime and suffering loss of sulfur as its primary property. However, if present, its lifetime in the gas phase above 100 °C is at most 10^{-4}–10^{-5} s.

Phenyl isothiocyanate, formed above ~100 °C, is the result of a process with an activation energy higher than that of the nitrile-forming reaction. It is most probably due to rearrangement with extrusion of nitrogen from the thioacyl azide in analogy with the Curtius rearrangement of acyl azides. However, rearrangements and concurrent extrusion of nitrogen from the thiatriazole cannot be directly excluded. It is currently believed that nitrenes are not intermediates in the Curtius rearrangement, or in the analogous Hofmann and Lossen rearrangements.[29]

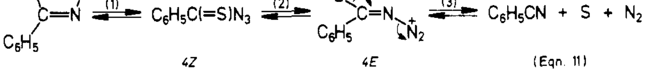
The stereochemistry of the proposed synchronous reaction without an intermediate thioacylnitrene does have consequences for the product formation. Thiobenzoyl azide may exist as two conformers (**4E** and **4Z**).



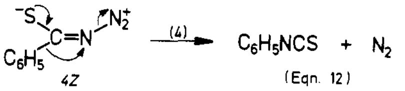
4E *4Z*

Benzonitrile may be formed by the following three-step mechanism with a trans fragmentation, a Grob-type fragmentation,[30] in the last step from the *E* conformer (eq 11). Phenyl isothiocyanate may be formed from the *Z* conformer in a Curtius rearrangement (eq 12).

Rotation around the C–N bond (**4Z–4E**) will probably be restricted because of partial double-bond character, and the energy barriers in steps 1 and 2 could be comparable.



4Z *4E* (Eqn. 11)



4Z (Eqn. 12)

Experimental Section

Mass Spectrometry. The investigations were performed with a Varian MAT CH 5 instrument equipped with a combined EI/FI/FD ion source. The samples were introduced in gold crucibles by the direct inlet system. The conditions for EI were the following: electron voltage, 70 eV; ionizing current, 100 µA; ion source temperature from 80 to 300 °C; probe temperature about 25 °C; resolution, ~1000. The appearance potentials were measured with an EI ion source with a trap current of 20 µA by variation of the electron accelerating voltage from 30 to 5 eV and using the semilog plot method. The ion source temperature was 270 °C, and the probe temperature was about 25 °C. The conditions for FI were the following: emitter (10 µm tungsten wire activated in benzonitrile vapor) current, 0 mA; and the voltage applied between the emitter and the cathode was about 8 kV. The ion beam was focused at the molecular ion from acetone at *m/e* 58.

Kinetic Measurements on the Thermolysis of 5-Aryl-1,2,3,4-thiatriazoles. Samples of 5-aryl-1,2,3,4-thiatriazoles (10^{-4} M in bromobenzene) were placed at 61.1 ± 0.1 °C in a Pye-Unicam SP1800 electronic absorption spectrometer equipped with a thermostat. The changes in absorption at 300 nm (in the case of 3-nitrophenylthiatriazole, at 294 nm) were recorded during the decomposition. First-order kinetics were obtained from the curves. Rate constants determined in the temperature range 52.2–61.1 °C were used to calculate activation parameters by a least-squares procedure: A = Arrhenius factor; E_a = activation energy; and $\Delta S^{\ddagger}$ = activation entropy.

Decomposition of 5-Phenyl-1,2,3,4-thiatriazole in the Presence of 1,3-Dipolarophiles. Samples ($\approx$ 5 mL) of a 0.05 M solution of 5-phenyl-1,2,3,4-thiatriazole[1] (1) in absolute ethanol containing 1,3-dipolarophiles (in a 3–5-fold excess) were heated to 60.0 ± 0.1 °C in closed tubes for 60 h for complete decomposition. The reaction mixtures were directly submitted to GLC on a Pye-Unicam 104 chromatograph, dual FID, connected to a Varian Aerograph 477 electronic integrator, using a 2 m × 0.5 in. column with 10% SE-30 on Gaschrom Q, 100–120 mesh (Applied Science Laboratory Inc.), with N_2 as the carrier gas. Yields were calculated on the basis of known amounts of 1 and an internal standard (benzyl cyanide) from integrated peaks upon comparison with calibration curves. Benzonitrile was detected in yields from 90.5 to 99.9%. An identical sample of pure 1 was treated similarly. Benzonitrile was detected in quantitative yield.

Catalyzed Decomposition of Phenylthiatriazole. To phenylthiatriazole (18.4 mmol) in benzene (100 mL) was added anhydrous aluminium chloride (4 × 1 g) with magnetic stirring at 20 °C over a period of 10 min. The first additions caused a very brisk evolution of nitrogen. The mixture was stirred at 20 °C for an additional 20 min and then hydrolyzed with ice (50 g). The benzene phase was washed with water (3 × 50 mL) and dried over $MgSO_4$. After removal of the solvent in vacuo, first at 15 mmHg and then at 0.1 mmHg and 30–40 °C, an oil was obtained (1.079 g) which was submitted to preparative TLC (benzene/silica gel). Five fractions were obtained: 1, 0.322 g; 2, 0.007 g; 3, 0.083 g; 4, 0.068 g; 5, 0.030 g. Fractions 3–5 were identified by infrared spectroscopy on comparison with authentic samples as benzonitrile (4.4%) (the yield may be higher because some material is most certainly lost due to evaporation), phenylthiatriazole (2.3%), and thiobenzamide (1.2%). Fraction 2 was not identified because of the small amount, and fraction 1 proved to comprise a mixture of diphenyl sulfide, benzyl phenyl sulfide, sulfur, and other compounds (combined GLC–mass spectrometry). Elemental analysis of fraction 1 gave the following result: C, 72.80; H, 5.75; N, 0.0; S, 21.75.

To phenylthiatriazole (~100 mg) in 5-mL flasks was added 5-ethoxythiatriazole (102.8, 191.0, and 422.5 mg), and the flasks were filled with dry ether. After 23 h, the ethoxythiatriazole had decomposed completely ($t_{1/2}$ = 2.15 ± 0.01 h[1]) and the solutions were evaporated to dryness to remove eventually formed benzonitrile at a temperature not exceeding 50 °C. Chlorobenzene (2 mL) and benzyl cyanide (~100 mg; as an internal standard) were added, and the mixture was heated to boiling for some minutes to convert phenylthiatriazole to benzonitrile. Benzonitrile was formed in quantitative yield within the limits of error (ca. ±2%), which shows that the sulfur generated from ethoxythiatriazole had not induced decomposition of phenylthiatriazole. Phenylthiatriazole was recovered practically unchanged (98%) from an ether solution left at room temperature for 24 h.

Reaction between Thiobenzoyl Chloride and Ammonium Azide at −115 °C Monitored by Electronic Absorption Spectroscopy. A. Solutions of thiobenzoyl chloride in ethanol were prepared at ca. −80 °C to avoid ester formation and transferred to a cooled UV cell.[31] The electronic absorption spectrum at −115 °C exhibited absorption at 526 nm, besides a shoulder at around 415 nm, while a more dilute solution exhibited absorptions at 315 and 295 nm. The 526 and 315 nm bands are assigned to thiobenzoyl chloride and the 415 and 295 nm bands to *O*-ethyl thiobenzoate. These values agree well with those reported previously at room temperature in cyclohexane for thiobenzoyl chloride (530, log $\epsilon \approx 2$, and 313 nm, log $\epsilon \approx 4$) and *O*-methyl thiobenzoate (418, log $\epsilon \approx 2$, and 287 nm, log $\epsilon \approx 2$).[10]

B. A solution (5 mL) of thiobenzoyl chloride in ethanol (4.2×10^{-4} M) was mixed in the UV cell with a solution (10 mL) of ammonium azide in ethanol (0.1 M) at −115 °C. The band at 526 nm (thiobenzoyl chloride; see A above) disappeared within 5 min on warming to around −100 °C. In another experiment, a reaction mixture that was a hundred times more dilute allowed observation in the short wavelength region of the formation of phenylthiatriazole (280 nm). In no case (concentrated or dilute reaction mixtures) were transient bands observed that could be ascribed to an intermediate in the sequence thiobenzoyl chloride/azide to phenylthiatriazole.

Phenylthiatriazole–$TiCl_4$ Complex. To phenylthiatriazole (250 mg) dissolved in benzene (10 mL; dried by filtration through neutral Al_2O_3, activity I, "Merck") was added $TiCl_4$ (250 μL), while the solution was purged with a slow stream of argon to protect it against atmospheric moisture. The solvent was removed from the precipitate by decantation, and after washing with a small amount of dry benzene and drying in vacuo an orange crystalline 1:1 complex (432 mg, 90% based on phenylthiatriazole) was obtained. This was extremely sensitive to moisture and immediately turned white on the surface on exposure to the atmosphere as a result of hydrolysis. On hydrolysis of the complex (432 mg) and extraction with ether, phenylthiatriazole (164 mg, 82%) was recovered. The molecular weight of the complex was estimated as 337 (calcd 353) by titration of the aqueous phase of the hydrolysate with silver nitrate according to the Volhard method. On heating, it decomposed at about 90 °C and melted at around 140 °C with rapid decomposition: IR (KBr) 1600 (s), 1510 (w), 1480 (s), 1460 (s), 1402 (s), 1374 (m), 1315 (w), 1240 (w), 1135 (w), 1030 (w), 998 (w). Extremely broad featureless absorptions were observed from 3600 to ~2800 cm^{-1} and from 900 to 400 cm^{-1}.

Irradiation of the Phenylthiatriazole–$TiCl_4$ Complex. The complex was prepared as above from 100 mg of phenylthiatriazole and dissolved in benzene (10 mL), and the solution was irradiated for 18 h with a medium-pressure Hg lamp through an acetone/anthracene filter ($\lambda > 390$ nm) while a slow stream of argon was led through the solution. After hydrolysis followed by extraction with benzene, almost pure phenylthiatriazole was isolated in 75% yield, which is close to the amount ordinarily recovered from the complex (see above). TLC of the benzene extract (benzene/silica gel) revealed, however, that small amounts of benzonitrile had been formed, but neither thiobenzamide nor *N*-phenylthiobenzamide was present.

Isotope Exchange Experiments. A. Phenylthiatriazole (99.8 mg) and $Na^{15}N_3$ (22.0 mg, 95% isotopically labeled on one N)[7] in C_2H_5OH/H_2O (8:2, 3 mL) were refluxed for 1.5 h. The solution was evaporated to dryness first at 12 mmHg (20–30 °C) and then at 0.1 mmHg (20–30 °C) to remove the benzonitrile that formed. The solid residue was extracted with ether, which on evaporation yielded 42.4 mg of phenylthiatriazole, corresponding to ~42% recovery. Mass spectrometry showed that all relevant ions ($M^{+\cdot}$ and $C_6H_5CN^{+\cdot}$) were accompanied by $(M + 1)^{+\cdot}$ ions in natural abundance; i.e., ^{15}N was present to the extent of 0.4% only. Therefore, ^{15}N had not been incorporated during decomposition of phenylthiatriazole.

B. Benzoyl azide (11.6 mg) and $Na^{15}N_3$ (5.3 mg; see A above) in C_2H_5OH/H_2O (8:2, 0.3 mL) were refluxed for 40 min. The solution was evaporated to dryness and extracted with C_2H_5OH/ether (1:1), which on evaporation yielded diphenylurea, identified by comparison of its infrared and mass spectra with an authentic sample. The mass spectrum of the *N,N'*-diphenylurea isolated exhibited the following ions with the relative intensities given in parentheses: *m/e* 214 (3), 213 ($(M + 1)^{+\cdot}$, 13), 212 ($M^{+\cdot}$, 23), 119 ($(M - C_6H_5NH_2)^{+\cdot}$, 8), 94 (27), 93 ($C_6H_5NH_2^{+\cdot}$, 100), 92 (7), 77 (8), 66 (12), 65 (8). Authentic diphenylurea exhibited a molecular ion (*m/e* 212) and a $(M + 1)^{+\cdot}$ ion with the calculated 15% intensity [13 × 1.1 (C) + 2 × 0.36 (N)] of the molecular ion. On this basis, we calculate the amount of ^{15}N in the isolated diphenylurea to be about 30%.

Decomposition of Phenylthiatriazole in the Presence of Sodium Hydroxide. Phenylthiatriazole (200 mg) was heated to reflux in a mixture of 2 N NaOH (3 mL) and ethanol (3 mL) for 10 min. After cooling, the mixture was extracted with ether (3 × 10 mL). The aqueous solution was purged with nitrogen to remove dissolved ether, and then it was added to a solution of carboxymethyl dithiobenzoate[1] (5×10^{-3} mol) in 1N NaOH (5 mL). After standing for 24 h, phenylthiatriazole had formed and was isolated in 4% yield based on the starting thiatriazole.

Acknowledgments. The authors wish to thank Professor E. Koch of the Max Planck Institute, Mühlheim, for the results of differential thermal analysis, Professor M. G. Ettlinger for valuable discussions, and Mrs. J. Funck and Mr. H. Egsgaard for their valuable technical assistance.

Registry No.—Phenylthiatriazole, 34733-85-2; 4-methoxyphenylthiatriazole, 67688-19-1; 4-methylphenylthiatriazole, 52098-71-2; 4-chlorophenylthiatriazole, 67688-20-4; 3-chlorophenylthiatriazole, 67688-21-5; 3-nitrophenylthiatriazole, 67688-22-6; aluminum chloride, 7446-70-0; thiobenzoyl chloride, 3335-22-6; ammonium azide, 12164-94-2; $TiCl_4$, 7550-45-0; phenylthiatriazole–$TiCl_4$

complex, 67722-21-8; [2-^{15}N]phenylthiatriazole, 67688-23-7; [4-^{15}N]phenylthiatriazole, 67688-24-8.

References and Notes

(1) (a) K. A. Jensen and C. Pedersen, *Adv. Heterocycl. Chem.*, **3**, 263 (1964); (b) A. Holm, *ibid.*, **20**, 145 (1976).

(2) H. E. Wijers, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **86**, 670 (1967).

(3) Cf. ref 4–6; R. Neidlein and J. Tauber, *Arch. Pharm.*, **304**, 687 (1971). Formation of nitrile sulfides via thiazirines and lack of thioacyl azide and thioacylnitrene transients in the photolytic conversion of thiatriazoles has been discussed elsewhere: A. Holm, N. Harrit, and I. Trabjerg, *J. Chem. Soc., Perkin Trans. 1*, 746 (1978) and references cited therein.

(4) K. A. Jensen and A. Holm, *Acta Chem. Scand.*, **23**, 2183 (1969).

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

(6) K. Pilgram, F. Görgen, and G. Pollard, *J. Heterocycl. Chem.*, **8**, 951 (1971).

(7) A. Holm, K. Schaumburg, N. Dahlberg, C. Christophersen, and J. P. Snyder, *J. Org. Chem.* **40**, 431 (1975).

(8) V. J. Shiner, Jr., *ACS Symp. Ser.*, **No. 11** (1975).

(9) (a) K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1104 (1961). (b) Experiments in this laboratory indicate that the optimal yield of thiatriazole by the carboxymethyl dithiobenzoate method is ~88%, which further indicates that at least less than 10% of the intermediate thiobenzoyl azide decomposes to benzonitrile (or undergoes solvolysis) instead of undergoing ring closure.

(10) The thiocarbonyl group is a characteristic chromophore; cf. J. Fabian, H. Viola, and R. Mayer, *Tetrahedron*, **23**, 4323 (1967).

(11) K. A. Jensen, S. Treppendahl, C. Christophersen, and G. Schroll, *Acta Chem. Scand., Ser B*, **28**, 97 (1974).

(12) K.-P. Zeller, H. Meier, and E. Müller, *Tetrahedron*, **28**, 1353 (1972).

(13) A. J. Jason and A. C. Parr, *Int. J. Mass Spectrom. Ion Phys.*, **22**, 221 (1976).

(14) H. D. Beckey, "Field Ionization Mass Spectrometry", Pergamon Press, New York, 1971.

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

(16) R. Okazaki, K. Okawa, S. Wajiki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **44**, 3167 (1971).

(17) A force constant of $K = 5.23$ mdyn/Å has been estimated for the S–N bond of 1,2,5-thiadiazole (O. Faurskov, private communication). Considering only the S(1)–N(2) stretch, we obtain from Bohr's frequency rule [$(1/2\pi c)\cdot(K/\mu)^{1/2}$; $\mu = m_1\cdot m_2/(m_1 + m_2)$] (B. Bak, "Elementary Introduction to Molecular Spectra", North-Holland Publishing Co., Amsterdam, 1962) $\nu_1(^{32}S-^{14}N) = 952$ cm^{-1} and $\nu_2(^{32}S-^{15}N) = 930$ cm^{-1}. On substitution in $k_1/k_2 = (\sinh hc\nu_1/2kT) \div (\sinh hc\nu_2/2kt)$, where $hc\bar{\nu}/2kT = 0.71929\bar{\nu}/T$ (ref 8, p 163), we estimate a maximum isotope effect of $k_1/k_2 = 1.048$ ($T = 353$ K). This value is expected to be diminished as a result of coupling of the S(1)–N(2) stretch with other vibrations of the molecule, but it is assumed to be significantly >1. A force constant of $K = 5.6$ mdyn/Å has been estimated for the N–N bond of 1,3,4-thiadiazole (O. Faurskov and P. A. Lund, private communication.). As above, we estimate a maximum isotope effect of $k_1/k_2 = 1.041$.

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

(19) Cf. W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969.

(20) A force constant of $K = 9.13$ mdyn/Å has been estimated for the N(1)–N(2) bond in phenyl azide (F. Nicolaisen, private communication, to be published.). Applying the procedure described in ref 17, we estimate a maximum isotope effect of $k_1/k_2 = 1.053$ ($T = 353$ K), and $\nu_1(^{14}N-^{14}N) = 1484$ cm^{-1} and $\nu_2(^{15}N-^{14}N) = 1459$ cm^{-1}. The Curtius rearrangement of benzoyl azide gives rise to an isotope effect in the bond breaking between N(1) and N(2) of 1.037: A. Fry and J. C. Wright, *Chem. Eng. News*, **46** (1), 28 (1968); J. C. Wright, Ph.D. Thesis, University of Arkansas, Fayetteville, Ark., 1966.

(21) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(22) A force constant of 16.6 mdyn/Å has been estimated for the N(2)–N(3) bond in phenyl azide (F. Nicolaisen, private communication, to be published.), and accordingly k_1/k_2 for the cleavage of this bond is 1.070.[17] From the Raman spectrum of N_2 (J. Bendtsen, *J. Raman Spectrosc.*, **2**, 133 (1974), $\nu = 2329.9$ cm^{-1}), k_1/k_2 is similarly calculated to be 1.080,[17] indicating only a small kinetic isotope effect connected with bond formation in the nitrogen extruded.

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

(24) R. G. McKenzie, Ed., "Differential Thermal Analysis," Vol. 1 and 2, Academic Press, New York, N.Y., 1970 and 1972; E. Koch, *Angew. Chem.*, **82**, 306 (1970); H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).

(25) E. Koch, *Chem. Ing. Tech.*, **44**, 111 (1972); "Non-Isothermal Reaction Analysis", Academic Press, London, 1977; H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957); E. Koch, *Angew. Chem.*, **85**, 381 (1973).

(26) E. Koch and B. Stilkerieg, *Thermochim. Acta*, **17**, 1 (1976).

(27) E. Koch, private communication, to be published.

(28) (a) W. Lwowski, "Nitrenes", Interscience, New York, 1970; (b) W. Lwowski, *Angew. Chem.*, **79**, 922 (1967); R. A. Abramovitch and B. A. Davies, *Chem. Rev.*, **64**, 149 (1964); L. Horner and A. Christmann, *Angew. Chem.*, **75**, 707 (1963); W. Kirmse, *Angew. Chem.*, **71**, 537 (1959).

(29) Cf. W. Lwowski, R. A. de Mauriac, M. Thompson, R. E. Wilde, and S.-Y. Chen, *J. Org. Chem.*, **40**, 2608 (1975), and references therein.

(30) C. A. Grob, *Angew. Chem.*, **81**, 543 (1969).

(31) The low temperature cell used is described elsewhere.[3]

Methylthiolation of 2,3-Bis(methylthio)butanes

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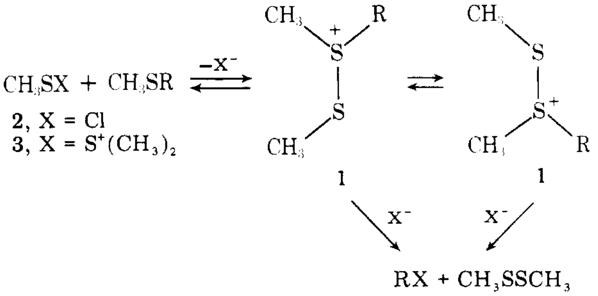
Received July 5, 1978

Reaction of dimethyl(methylthio)sulfonium fluoroborate with *meso*- and *dl*-2,3-bis(methylthio)butane appears to be a straightforward methylation of the sulfide to give a sulfonium salt of *retained* configuration. However, the product is actually formed in a multistep reaction involving C–S cleavage in the starting sulfide rather than in the starting salt. The initial step involves methylthiolation of 2,3-bis(methylthio)butane by the salt. This step reversibly forms methyl sulfide and a thiosulfonium ion that dissociates reversibly and stereospecifically to methyl disulfide and a thiiranium (episulfonium) ion with the result that methylthio exchange occurs. The thiiranium ion intermediate is trapped irreversibly by methyl sulfide to give the observed products of retained configuration.

In a previous study on the reaction of sulfides with sulfenyl compounds, we reported a degenerate rearrangement of an alkylthiosulfonium ion **1**.[1] For example, an ion of this type is evidently formed as an intermediate in the reaction of methyl 1-phenylethyl sulfide with methylthiolating agents such as methanesulfenyl chloride (**2**) and dimethyl(methylthio)sulfonium fluoroborate (**3**) (eq 1). The intermediate **1** is formed rapidly and reversibly in a displacement reaction at the sulfenyl sulfur of **3**.[2-4] Subsequently, **1** reacts irreversibly with the displaced nucleophile X to give the observed products. The rearrangement step was inferred from labeling studies in which a SCD_3 group in the starting sulfide was found to exchange with the SCH_3 group of the sulfenyl reagent. A further observation that is central to the objectives of the current investigation was that reaction of **3** with the (+) en-



(1)