as above gave benzamide, 0.17 g; benzophenone, 0.48 g (purified as the 2,4-dinitrophenylhdyrazone); benzoic acid, 0.12 g; and unreacted 13, 0.09 g.

Reaction of *N*-Benzylhydroxylamine with Potassium Hydroxide in *tert*-Butyl Alcohol. The procedure above was repeated using 1.00 g of *N*-benzylhydroxylamine.[13] The neutral fraction was examined by IR and NMR and found to contain neither benzaldehyde nor benzyl alcohol.

Acknowledgment. We would like to thank Dr. Cal Meyers, whose work on the *tert*-butyl alcohol–potassium hydroxide system inspired much of this work.

Registry No.—7, 61267-53-6; dimethyl sulfoxide, 67-68-5; *N*-benzyl-α-phenylnitrone, 3376-26-9; *tert*-butyl alcohol, 75-65-0; potassium hydroxide, 1310-58-3; tetraphenylpyrazine, 642-04-6; deoxybenzoin, 451-40-1.

References and Notes

(1) J. H. Hall and M. Gisler, unpublished results.
(2) H. E. De La Mare and G. M. Coppinger, *J. Org. Chem.*, **28**, 1068 (1963).
(3) R. Bonnett, V. M. Clark, and A. Todd, *J. Chem. Soc.*, 2102 (1959).
(4) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).
(5) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958).
(6) G. E. Utzinger and F. A. Regenass, *Helv. Chim. Acta*, **37**, 1892 (1954).
(7) R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2109 (1959).
(8) R. F. C. Brown, V. M. Clark, M. Lamchen, and A. Todd, *J. Chem. Soc.*, 2116 (1959).
(9) F. H. Banfield and J. Kenyon, *J. Chem. Soc.*, 1612 (1926).
(10) L. Chardonnes and P. Heinrich, *Helv. Chim. Acta*, **27**, 321 (1944).
(11) R. Huisgen, E. Funke, H. Gotthard, and H. L. Panke, *Chem. Ber.*, **104**, 1532–1549 (1971).
(12) A. M. Simonox, A. D. Garnovskii, Yu. N. Sheinker, B. I. Khristich, and S. S. Trofimora, *Zh. Obshch. Khim.*, **33**, 571–579 (1963).
(13) H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *J. Org. Chem.*, **30**, 2877 (1965).

Thermal Decomposition of 1-Phenyl-3,3-ethylenetriazenes[1]

Rosalind E. Clark and Ronald D. Clark*

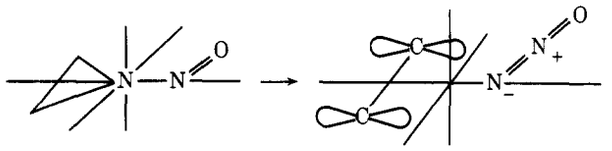
Department of Chemistry, New Mexico Highlands University, Las Vegas, New Mexico 87701

Received February 3, 1976

Upon warming to room temperature, *cis*- or *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene decomposes to form *cis*- or *trans*-2-butene and phenyl azide with retention of configuration. The decomposition reaction is first order, with an activation energy of 32 kcal/mol. Low-temperature NMR studies suggest that there is a hindered rotation in the trans compound with an activation energy of 5.7 kcal/mol. A mechanism has been proposed for the decomposition reaction that is consistent with orbital symmetry rules.

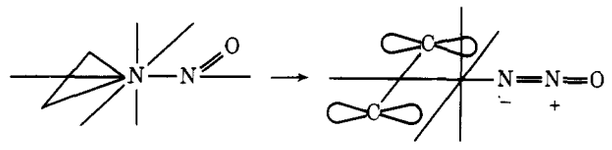
Ethylenediazene and *N*-nitrosoaziridine have been reported to be unstable, decomposing below room temperature to form ethylene and the corresponding inorganic compound.[2] In both cases the reaction has been reported to be stereospecific with retention of configuration.[2a,3]

Woodward and Hoffman[4] have considered these two systems from the viewpoint of orbital symmetry. They concluded that both reactions proceed by a nonlinear pathway in which the nonbonding electron pair on the nitrogen atom originally in the ring comes from the antisymmetric molecular orbital of the triazene. In the case of the nitrosamine, they recognized two possible pathways by which this could take place. In the first pathway (mechanism A), the nitrous oxide molecule was



Mechanism A

visualized as leaving orthogonal to the plane bisecting the aziridine ring. In the second pathway (mechanism B), the

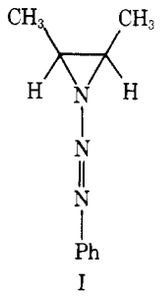


Mechanism B

nitrous oxide molecule was visualized as remaining in the plane bisecting the aziridine ring.

With little direct experimental data available, Woodward and Hoffman suggested that mechanism A was more probable than mechanism B. This suggestion was based on the observation that the barrier to rotation in dimethylnitrosamine is 23 kcal/mol[5] while the barrier to decomposition of *trans*-2,3-dimethyl-*N*-nitrosoaziridine is only 16 kcal/mol.[2a] To the extent that it is valid to extrapolate from dimethylnitrosamine to *N*-nitrosoaziridine, it appears that the compound would decompose before it could achieve the correct conformation for mechanism B.

Because of the lack of direct experimental evidence concerning the difference between mechanisms A and B, we felt that it would be enlightening to investigate another cheletropic three membered ring decomposition. We chose the thermal decomposition of 1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene (I) because it could be isolated and purified, it



I

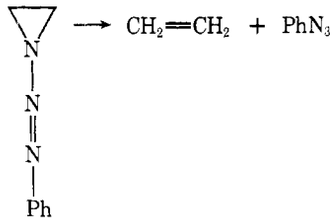
decomposed readily, and no stereochemical or mechanism work had been reported.

Preparation of 1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene. Phenyl-substituted ethylenetriazenes were first reported by Rondestvedt and Davis,[6] who found that they were unstable, decomposing to form ethylene and phenyl azide

Table I. 2-Butene Distribution from the Decomposition of *cis*- and *trans*-1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene

Solvent	Starting material	% yield	% *cis*-2-butene	% *trans*-2-butene
Carbon tetrachloride	Trans triazene	95	2.2	97.8
	Cis triazene	91	94.4	5.6
p-Xylene	Trans triazene	5	3.4	96.6
	Cis triazene	92	94.2	5.8
Acetone	Trans triazene	82	6.8	93.2
	Cis triazene	80	93.8	6.2
N,N-Dimethyl-formamide	Trans triazene	71	15.9	84.1
	Cis triazene	75	82.9	17.1
p-Dioxane	Trans triazene	5	17.2	82.8
	Cis triazene	5	80.7	19.3
2-Propanol	Trans triazene	66	20.1	79.9
Water	Trans triazene	77	23.3	76.7
	Cis triazene	74	87.8	12.2

upon warming to room temperature. They did not investigate the mechanism of the reaction, however.



In the present study, stereospecific *cis*- and *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazenes were prepared from the corresponding *cis*- and *trans*-2,3-dimethylaziridines[7] and benzenediazonium chloride by a modification of the procedure of Rondestvedt and Davis.[6] While the compounds appeared to be completely stable at −78 °C, they were unstable at room temperature. As a consequence, structure proof was limited to instrumental techniques. All of the compounds studied exhibited consistent infrared, nuclear magnetic resonance, and ultraviolet–visible spectra.

Stereochemical Course of Decomposition. The thermal decomposition of *cis*- and *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene was carried out in several solvents by adding the compounds to the cooled solvent and then heating the mixture to reflux temperature. The gaseous butenes were collected in a dry ice trap, and analyzed by gas chromatography. The results are shown in Table I.

The decomposition reaction was stereospecific with retention of configuration in nonpolar solvents. Some loss of stereospecificity was observed in polar solvents. The loss of stereospecificity was probably caused by a competing ionic reaction. This competition was suggested by the lower 2-butene yields in the polar solvents. A reproducible low yield of butene was also observed for *cis*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene in *p*-xylene. This phase of the problem will be explored further in a later paper.

Rate of Decomposition. The rate of decomposition was followed using NMR spectroscopy by observing the rate of disappearance of the starting material. Other techniques such as ultraviolet spectroscopy and polarography could not be used because the products formed interfered with the measurement of the starting materials. The methyl doublet in *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene occurred at δ 0.98 ppm from Me_4Si, which was adequately separated from the *trans*-2-butene doublet at δ 1.28 ppm. Similarly, the methyl doublet in *cis*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene occurred at δ 0.84 ppm while the methyl doublet in *cis*-2-butene occurred at δ 1.30 ppm.

Table II. Rate of Decomposition of *cis*- and *trans*-1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene

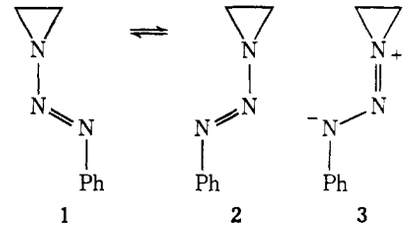
Compd	Temp °C	$k \times 10^2$, min^{-1}	Half-life, min
Trans triazene	20.0	0.77 ± 0.01	90
Trans triazene	25.1	2.09 ± 0.02	33
Trans triazene	29.7	4.34 ± 0.11	15.5
Cis triazene	19.8	2.69 ± 0.22	25

The rate studies were conducted in methylene chloride solvent containing 4% Me_4Si as a reference. The field was locked to the methylene chloride band to prevent drift, and spectra were taken at 5- or 10-min intervals. The temperature was calibrated by measuring the chemical shift in methanol. The results are shown in Table II.

As expected, the decomposition reaction was first order in triazene. Based on the rate constants in Table II, the Arrhenius activation energy for the decomposition of *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene was 32 kcal/mol. The entropy of activation was 29 eu, an unexpectedly large value.

Low-Temperature NMR Studies. At low temperature the alkyl portion of the NMR spectrum of *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene was observed to split into two sets of bands which coalesced at −45 °C. Spectra were taken from −76 to −45 °C, and by measuring the splitting and utilizing the method of Gutowsky and Holm,[8] the activation energy for the process was calculated to be 5.7 kcal/mol. The corresponding cis compound did not exhibit this phenomenon.

The low-temperature NMR spectra suggest that there is a barrier to rotation about the N–N single bond in the trans triazene. This barrier is probably best explained by a rapid equilibrium between conformations **1** and **2**. The barrier is



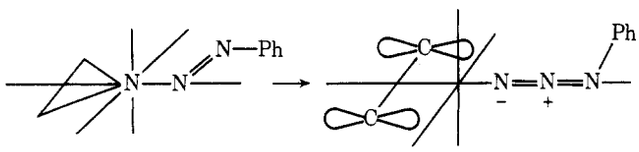
probably due to significant contribution from resonance structures related to **3**. Marullo, Mayfield, and Wagener[9] have observed a similar barrier to rotation in 1-phenyl-3,3-dimethyltriazene of 12.7 kcal/mol.

Discussion

Since product formation is stereospecific, and the reaction is first order in triazene, the transition state probably involves a concerted cleavage of the two C–N bonds. A mechanism similar to either mechanism A or B would be appropriate for this system.

The principle of least motion would suggest that a mechanism like B should be preferred over mechanism A since the large PhN=N– group would have to move further to form an orthogonal activated complex than to form a linear activated complex. Since the activation energy for inversion (5.7 kcal/mol) is considerably smaller than the activation energy for decomposition (32 kcal/mol), the molecule may be expected to pass through a linear conformation many times before decomposing. Also, the high entropy of activation for the decomposition reaction suggests that no significant reorganization is required in going from the ground state to the tran-

sition state. These reasons, while not conclusive, suggest to us that the following mechanism may not only be possible, but



actually be preferred. This mechanism is similar to mechanism B for the decomposition of *N*-nitrosoaziridine.

Woodward and Hoffman preferred mechanism A for the decomposition of *N*-nitrosoaziridine because the barrier to rotation in dimethylnitrosamine (23 kcal/mol), which they hoped was similar to *N*-nitrosoaziridine, was greater than the barrier to decomposition of *trans*-2,3-dimethyl-*N*-nitrosoaziridine (16 kcal/mol). In an effort to check this assumption, we prepared a sample of *trans*-2,3-dimethyl-*N*-nitrosoaziridine and studied its NMR spectrum between −20 and −80 °C. No evidence could be seen for hindered rotation at any temperature studied. For this reason, we have concluded that there is no significant barrier to rotation in the *N*-nitrosoaziridine system, and that mechanism B is possibly the correct mechanism for both the *N*-nitroso and triazene systems.

Experimental Section

Pure (99%) *cis*- and *trans*-2-butenes were obtained from Matheson Gas Products, La Porte, Texas. *cis*- and *trans*-2,3-dimethylaziridines were prepared from the corresponding butene via the epoxide using the procedures of Dickey, Fickett, and Lucas.[7] This sequence has been shown[2a,7] to be greater than 99% stereospecific.

NMR spectra were run on a Varian Model T-60A nuclear magnetic resonance spectrometer equipped with a lock decoupler and for variable temperature operation. Gas chromatographic analyses were run on either a Beckman Model GC-2 or a Carle Model 8000 gas chromatograph.

Preparation of *cis*- and *trans*-1-Phenyl-3,3-(2,3-Dimethyl)-ethylenetriazene. Sodium nitrite (5.2 g, 0.075 mol) dissolved in 15 ml of distilled water was added dropwise to aniline (7.0 g, 0.075 mol) which had been dissolved in 75 ml of 3 N hydrochloric acid (0.225 mol) at 0–5 °C. The reaction mixture was maintained at 0–5 °C during the addition. Sodium acetate (12.5 g, 0.15 mol) was then added and the reaction mixture cooled to −5 to −10 °C. *trans*-2,3-Dimethylaziridine (9.0 g, 0.15 mol) was added dropwise and immediately followed by the addition of 12.3 g (0.15 mol) of sodium acetate. While maintaining the reaction mixture at about −10 °C, 35 ml of cold (about 5 °C) pentane was added to the reaction mixture. After stirring, the pentane layer was decanted off and the reaction mixture extracted twice more with pentane. The pentane extracts were immediately cooled in a dry ice–2-propanol bath. The resulting yellow crystals (8.7 g, 0.050 mol, 66% yield) were separated by filtration at 0–5 °C and stored in a Dewar filled with dry ice: ^{1}H NMR ($CDCl_3$) δ 0.98 (6 H, d), 2.01 (2 H, m), 7.10 (5 H); IR 1605 (s) (Ph), 1596 (s) (Ph or N=N), 1478 (s), 1445 (s), and 1380 cm^{-1} (s). The triazene system lacks characteristic bands. As the compound decomposed, the characteristic bands of phenyl azide, 2150 (s), 2140 (m), and 1250 cm^{-1} (s), appeared.

The trans compound absorbed strongly in the visible region at 354 nm and had bands in the ultraviolet region at 300 (sh), 225 (sh), and 230 nm. Literature values[10] for the ultraviolet spectral bands of 1-phenyl-3,3-dimethyltriazene were 308 (sh), 285, and 225 nm.

Using the above procedure, the *cis*-1-phenyl-3,3(2,3-dimethyl)-ethylenetriazene was prepared using the *cis*-2,3-dimethylaziridine. The triazene was obtained in a 66% yield (8.7 g, 0.050 mol): ^{1}H NMR ($CDCl_3$) δ 0.84 (d, 6 H) 2.38 (m, 2 H) 7.13 (5 H).

Decomposition of 1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene. In a typical run, 1.5 g (0.0086 mol) of *cis*- or *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene were dissolved in 25 ml of reagent grade carbon tetrachloride. The two-necked flask was fitted with a magnetic stirrer and a condenser leading to a collection tube immersed in a dry ice–2-propanol bath. The reaction mixture was heated at reflux for 30 min during which time the yellow solution darkened and 0.46 g (0.0083 mol, 95%; lower yield for cis compound) of 2-butene was collected. The products collected were analyzed for *cis*- and *trans*-2-butene by gas chromatography (25 ft 30% GESF-96 Silicone Oil on firebrick at room temperature).

Table III. NMR Splittings at Various Temperatures for *trans*-1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene

Temp, °C	δ_{CO}	Log $(1/\tau\delta\omega)$
−76	48	
−69	46.5	−0.762
−67	46.5	−0.762
−61	45	−0.606
−57.5	42.0	−0.466
−51	32	−0.278
−49	27	−0.232
−46.6	18	−0.184
−45	0	

The same procedure was used in decomposing *cis*- or *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene in the other solvents listed in Table I. All were heated at reflux or at 50–60 °C for 30 min or until no more butene could be collected.

Low-Temperature NMR Spectral Studies. Low-temperature NMR studies were carried out using a 4-mm NMR tube and liquid nitrogen cooling. The same methylene chloride solvent containing 4% Me_4Si that had been prepared for the kinetic studies was used. The field was locked to the methylene chloride band to prevent drift and facilitate tuning at low temperature.

Spectra were run at various temperatures from about −20 °C to −80 °C. Only the trans triazene showed any observable temperature effect as already described. The splittings at various temperatures are given in Table III.

Kinetic Studies. The rate of decomposition of *cis*- and *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene was determined from the alkyl region of the NMR spectrum. Spectra of this region were run at either 5- or 10- min intervals, and the change in area of the methyl doublet of the triazene determined as a function of time. The reaction followed a first-order rate law, and the rate constant was determined via computer analysis of the data.

The temperature range studied was determined by the practical limitations of the experimental method. At temperatures much lower than 20 °C, the reaction was so slow that it was impossible to keep both the temperature and the tuning of the instrument constant over the length of the run. At temperatures much above 30 °C, the reaction was so fast that the peaks could not be scanned fast enough to get accurate area data. A wider temperature range would have been desirable.

Methylene chloride was selected as the solvent so that the field could be locked to the solvent band to prevent drift. Me_4Si (4% by volume) was added to the solution as an internal integration standard. The instrument was found to be so stable, however, that correction of the data was not necessary.

Acknowledgments. The authors wish to thank the Institute of Research at New Mexico Highlands University for financial support of this project. We also wish to thank Dr. Mohamed Alei at the Los Alamos Scientific Laboratories and Dr. William Litchman and Mr. Charles Milner at the University of New Mexico for assistance with some of the preliminary NMR spectra. We are also indebted to the National Institutes of Health Minority Biomedical Support Program for purchasing the NMR instrument which made the completion of this project finally possible.

Registry No.—*cis*-1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene, 61268-03-9; *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene, 61268-04-0; *trans*-2,3-dimethylaziridine, 930-20-1; *cis*-2,3-dimethylaziridine, 930-19-8; aniline, 62-53-3.

References and Notes

(1) Presented in part at the First Rocky Mountain Regional Meeting of the American Chemical Society, Fort Collins, Colo., June 28, 1972.
(2) (a) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964); (b) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963).
(3) J. P. Freeman and W. H. Graham, *J. Am. Chem. Soc.*, **89**, 1761 (1967).
(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781–853 (1969).

(5) C. E. Looney, W. D. Phillips, and E. L. Reilly, J. Am. Chem. Soc., 79, 6136 (1957).
(6) C. S. Rondestvedt and S. J. Davis, J. Org. Chem., 22, 200 (1957).
(7) F. H. Dicky, W. Fickett, and H. J. Lucas, J. Am. Chem. Soc., 74, 944 (1952).
(8) H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 24, 1228 (1956).
(9) N. P. Marullo, C. B. Mayfield, and E. H. Wagener, J. Am. Chem. Soc., 90, 510-511 (1968).
(10) R. J. W. Le Fevre and T. H. Liddicott, J. Chem. Soc., 2743-2748 (1951).

Thermal Rearrangement of O-(2,4,6-Trihalophenyl) N,N-Dimethylthiocarbamates. An Abnormal Pathway[1]

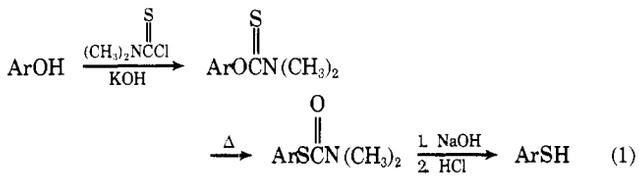
Charles E. Reineke* and Christian T. Goralski

Halogens Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

Received March 29, 1976

The conversion of phenols to benzenethiols via the N,N-dimethylthiocarbamates has been applied to the 2,4,6-trihalophenols. Results were highly dependent on whether the halogen was Cl, Br, or I. The pyrolysis of O-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (1) yielded S-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (2) which on hydrolysis gave 2,4,6-trichlorobenzenethiol (3). The pyrolysis of O-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (4) gave 78% of S-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (5) and 22% of N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)methanamine (6). Hydrolysis of this reaction mixture gave 2,4,6-tribromobenzenethiol (7) and bis(3,5-dibromo-2-hydroxyphenyl) disulfide (8). Compound 6 was shown to arise from N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium bromide (9), which was isolated as an intermediate. The pyrolysis of O-(2,4,6-triiodophenyl) N,N-dimethylthiocarbamate (13) gave 80% of N-(5,7-diiodo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium iodide (14). A mechanism is described.

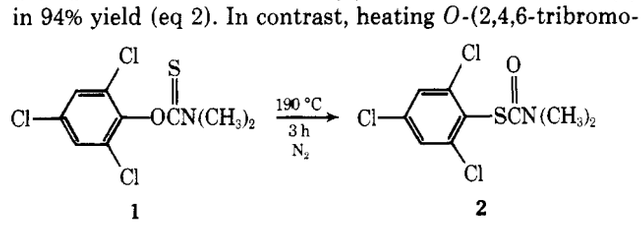
In 1966, Newman and Karnes[2] described a general method for the conversion of a phenol to the corresponding thiophenol which involved (a) reaction of the phenol with potassium hydroxide and dimethylthiocarbamoyl chloride to give the O-(aryl) N,N-dimethylthiocarbamate, (b) thermal rearrangement of the O-(aryl) N,N-dimethylthiocarbamate to the S-(aryl) N,N-dimethylthiocarbamate, and (c) hydrolysis of the S-(aryl) N,N-dimethylthiocarbamate to the thiophenol (eq 1).[3] More recently, this reaction sequence was applied to



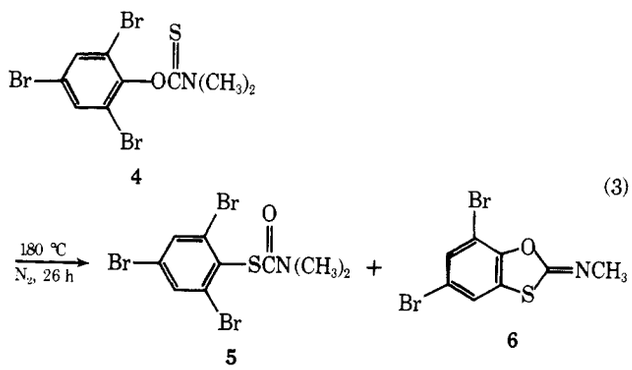
(1)

the preparation of the three isomeric tetrachlorobenzenethiols by Goralski and Burk[4] and to the synthesis of 2-mercaptophenol by Dodson and Hanson.[5] In this paper we discuss the thermal rearrangement of O-(2,4,6-trihalophenyl) N,N-dimethylthiocarbamates.

Pyrolysis of O-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (1) at 190 °C in a nitrogen atmosphere for 3 h afforded an 82% yield of S-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (2).[6] Hydrolysis of 2 with sodium hydroxide in methanol afforded 2,4,6-trichlorobenzenethiol (3) in 94% yield (eq 2). In contrast, heating O-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (4) at 180 °C in a nitrogen atmosphere for 26 h afforded 78% S-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (5) and 22% N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)methanamine (6, eq 3).



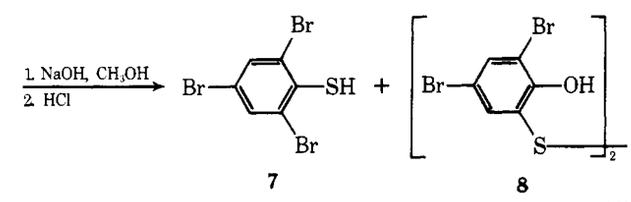
(2)



(3)

Subsequent hydrolysis of this product mixture with sodium hydroxide in methanol and fractional recrystallization of the acidified product gave 2,4,6-tribromobenzenethiol (7) in 69% yield, and bis(3,5-dibromo-2-hydroxyphenyl) disulfide (8) in 8% yield (eq 4). The structure of 8 was proven by reduction to

5 + 6



(4)

2,4-dibromophenol with Raney nickel. When the rearrangement of 4 was run at 170 °C, an insoluble material, isomeric with 4, was isolated and shown to be N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium bromide (9). The structure of 9 was confirmed by hydrolysis with 1 N sulfuric acid to give 5,7-dibromo-1,3-benzoxathiol-2-one (10a), and by hydrolysis in basic solution to give 2,4-dibromo-6-