Pyrolysis and Mass Spectra of the 2-Thiones of Benzothiazole, Benzimidazole, and Benzoxazole

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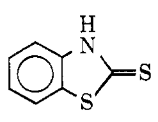
Received October 25, 1972

The electron-impact and chemical-ionization mass spectra of benzothiazole-2-thione (**1**), benzimidazole-2-thione (**2**), and benzoxazole-2-thione (**3**) have been compared with those of their pyrolysis products and parallels have been found. In each case, the loss of S from the molecular ions and from the (M + H) ions is the lowest energy fragmentation. At 800°, **1** gives a 23% yield of benzothiazole (**4**) and a 13% yield of cyanobenzene (**5**). Loss of S accounts for the formation of **4**. Compound **5** arises from **1** by loss of S_2 and from **4** by loss of S. The one-step loss of S_2 is observed also in the mass spectrum of **1**. At 950°, **2** gives 62.5% of benzimidazole (**6**) and 7.5% of 2-cyanoaniline (**8**), which are formed from the loss of S from **2** and rearrangement of **6** to **8**. At 1000°, **3** gives 1.3% of benzoxazole (**10**) and 38% of 2-cyanophenol (**11**) from the loss of S. Compound **10** is readily converted to **11** at 1000°. Compound **3** also gives 12 and 15% of 1- and 2-cyanonaphthalene (**13** and **14**), respectively, and 7% of naphthalene, presumably by an initial loss of COS from **3**, a low-energy loss also observed in the mass spectrum.

As part of a series of studies[2,3] in which we compare the formation of pyrolysis products with mass spectral fragmentations of organic molecules, we wish to report results obtained from benzothiazole-2-thione (**1**), benzimidazole-2-thione (**2**), and benzoxazole-2-thione (**3**).



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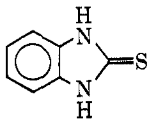

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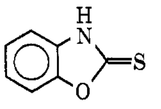


3

These thiones have been pyrolyzed at a variety of temperatures with the aim of observing the effect of temperature on the distribution of products. When it was deemed necessary, methanol was introduced into the system as an agent for trapping radicals and high-energy intermediates. Also, whenever possible, we pyrolyzed compounds which were identified in the pyrolysis mixtures from **1**–**3**, in order to see if other products arise from them by secondary pyrolysis.

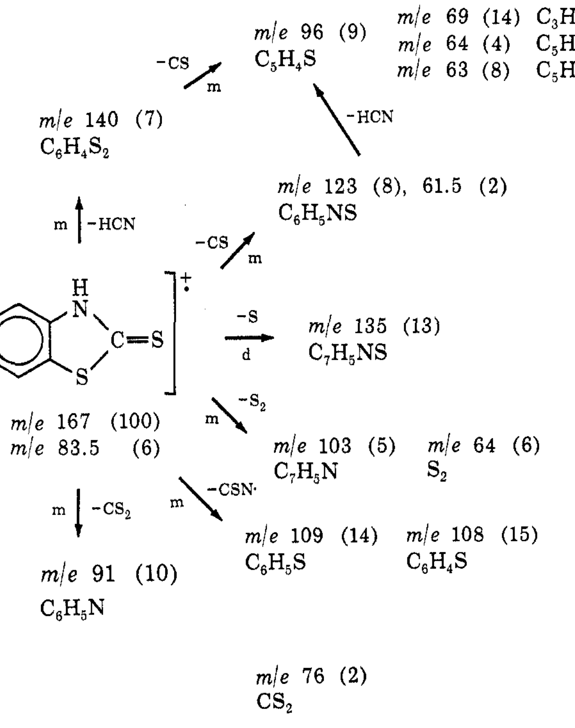
Extensive studies using, for example, ir[4] and ^{14}N nmr[5] techniques have shown that **1** exists in the thione form rather than in the tautomeric thiol form, both in the solid and in solution. Similar results have been obtained from studies on **2**[6] and **3**.[7] We do not know which form is present under our conditions of pyrolysis and in the mass spectrometer. However, our results can better be discussed in terms of the thione form; thus it will be used in the figures and schemes.

The mass spectra of **1**[8] and **2**[9] have been published previously. The mass spectrum of **3** is given in Figure 1. High-resolution data and metastable transitions are given in the schemes for the three compounds. Certain features of the mass spectra taken at low ionizing voltages are presented in the text. Chemical ionization mass spectra are discussed in the case of compounds **1** and **3**.

Results and Discussion

Benzothiazole-2-thione (**1**).—The 70-eV mass spectrum of benzothiazole-2-thione (**1**) is summarized in Scheme I. The elimination of S (*m/e* 167 → 135) from the molecular ions is the only fragmentation when the electron voltage is lowered below 15 eV. Metastable transitions were detected for this loss of S and for the loss of S_2 (*m/e* 167 → 103); however, no metastable peak is detectable for the loss of S from *m/e* 135, which would give *m/e* 103 from the molecular ions by a two-

Scheme I[a]



[a] m denotes a metastable peak in the mass spectrum; d denotes the detection of a metastable transition when the instrument is operated in the defocused mode; the elemental compositions result from exact-mass measurements; the values in parentheses are relative intensities.

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(2) D. C. DeJongh and G. N. Evenson, *J. Org. Chem.*, **37**, 2152 (1972), and references cited therein.

(3) D. C. DeJongh and R. Y. Van Fossen, *Tetrahedron*, **28**, 3603 (1972).

(4) H. Larivé, A. J. Chambonnet, and J. Metzger, *Bull. Soc. Chim. Fr.*, 1675 (1963).

(5) A. Mathias, *Mol. Phys.*, **12**, 381 (1967).

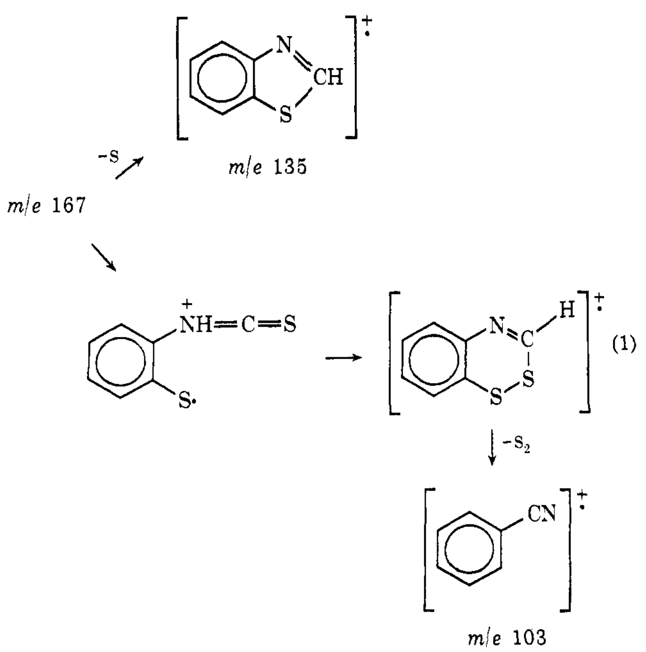
(6) P. Nuhn, G. Wagner, and S. Leistner, *Z. Chem.*, **9**, 152 (1969).

(7) N. L. Aryutkina, A. F. Vasil'ev, N. A. Poznanskaya, N. I. Shvetsov-Shilovskii, S. N. Ivanova, and N. N. Mel'nikov, *Zh. Obshch. Khim.*, **40**, 1872 (1970).

(8) B. J. Millard and A. F. Temple, *Org. Mass Spectrom.*, **1**, 285 (1968).

(9) H. Lund and L. G. Feoktistov, *Acta Chem. Scand.*, **23**, 3482 (1969).

step process. Possible rationals for the loss of S and S_2 from m/e 167 are given in eq 1; the ions corresponding

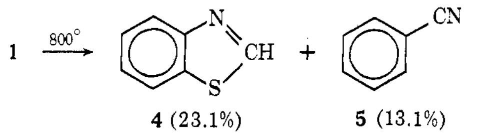


to the molecular ions of benzothiazole (**4**) and cyanobenzene (**5**) are shown as possibilities for m/e 135 and 103. Other fragmentations of the molecular ions of **1** involve losses of molecules and radicals from the heterocyclic ring, such as CS, CS_2, HCN, and CNS·. The mass spectrum of the closely related *o*-phenylene trithiocarbonate has been published and discussed.[10]

In the chemical ionization mass spectrum the (M + H) ion (m/e 168, 100%) and the (M + H − S) ion (m/e 136, 6%) are the only prominent peaks associated with **1**. In this case also, the loss of S is a low-energy path.

We were interested in trying to duplicate some of these losses from the molecular ions of **1** by means of thermal excitation. Therefore, we pyrolyzed **1** by subliming it in a stream of N_2 through a zone heated by an electric furnace. The apparatus and procedure are described in the Experimental Section. A range of temperatures (700–950°) was used; the details are given in the Experimental Section.

The pyrolysis products from **1** are benzothiazole (**4**) and cyanobenzene (**5**), eq 2. The percentages of **4** and



4 (23.1%) 5 (13.1%) (2)

5 varied with the temperature used; the formation of **5** is favored at higher temperatures. In order to determine whether or not **5** forms from secondary pyrolysis of **4**, we pyrolyzed **4** under the same conditions that we had pyrolyzed **1**. At 750°, 64% of **4** was recovered and 0.6% of **5** was isolated; however, at 950°, only 7% of **4** was recovered and 44% of **5** was obtained. Thus, it is likely that **5** forms directly from pyrolysis of **1**, as well as from a secondary pyrolysis of **4**.

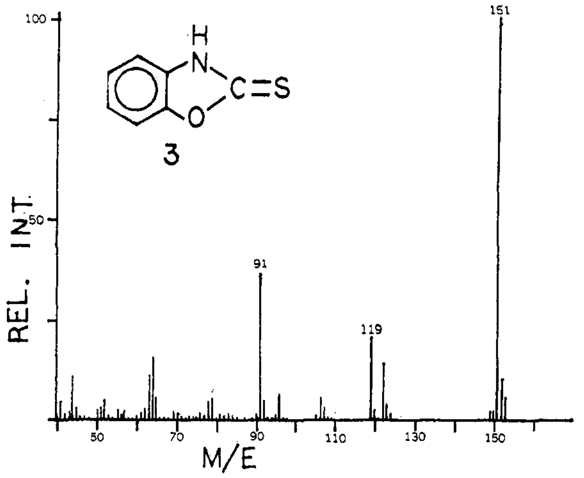


Figure 1.—Mass spectrum (70 eV) of benzoxazole-2-thione (**3**).

We used eq 3 in order to relate the pyrolyses of **1** and of **4**. Although the equation ignores conventional

$$\frac{A}{A + B} = \frac{D - X}{C + D - X} \qquad (3)$$

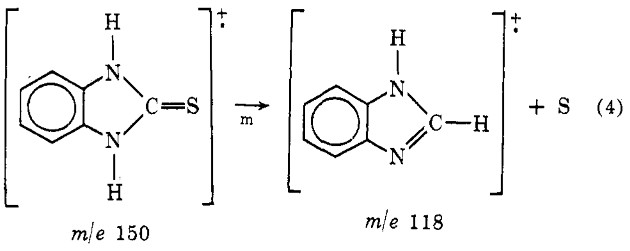
kinetics, it gives a crude idea of the relative amount of **5** which forms directly from **1** and the amount which forms indirectly from **1** *via* secondary pyrolysis of **4**. The term A equals the per cent of **5** formed from **4** in the pyrolysis of **4** and B represents the per cent of **4** recovered from the pyrolysis of **4**. The per cent of **4** isolated from the pyrolysis of **1** is C; D is the per cent of **5** isolated from the pyrolysis of **1**. The unknown quantity X is the per cent of **5** formed directly from **1** *via* a one-step process and $D - X$ is the per cent of **5** from **1** *via* the two-step path.

Using the results in the Experimental Section from the pyrolyses of **1** and **4**, at 750°, we calculated X and $D - X$. At 750°, a yield of 4.6% of **5** is formed from **1**; of this 4.4% is from the one-step path and 0.2% from the two-step path. At 900°, a yield of 34.1% of **5** is formed from **1**; of this 17.6% comes from the one-step path and 16.5% from the two-step path.

Thus, the formation of the pyrolysis products can be explained by the same competing paths observed in the mass spectrum (eq 1): the molecules lose S or S_2. In addition, at high temperatures, a further pyrolysis of **4** begins, giving **5** *via* two steps from **1**.

Benzimidazole-2-thione (**2**).—The 70-eV mass spectrum of benzimidazole-2-thione (**2**) is summarized in Scheme II.

The lowest energy path, *i.e.*, the only path to survive below 14 eV, is the loss of S, giving m/e 118. This fragmentation is accompanied by a metastable peak. The ions at m/e 118 probably correspond to the molecular ions of benzimidazole (**6**) (eq 4).



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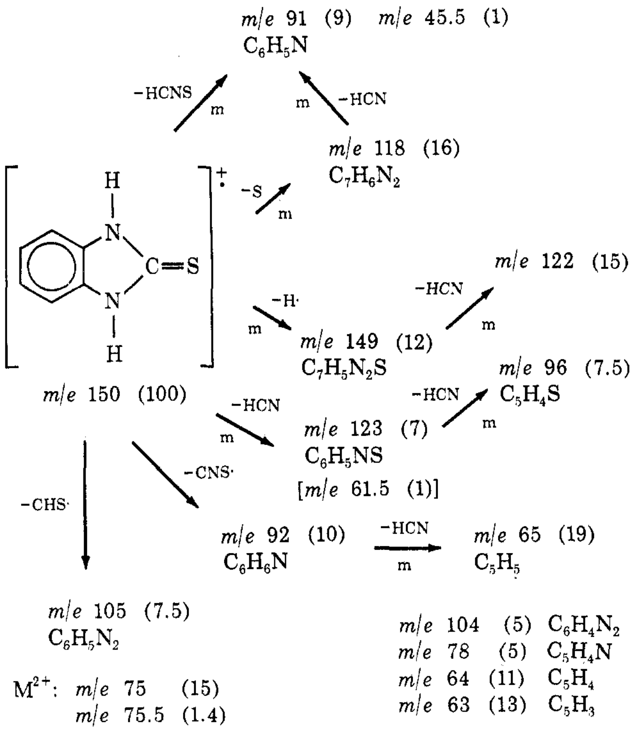
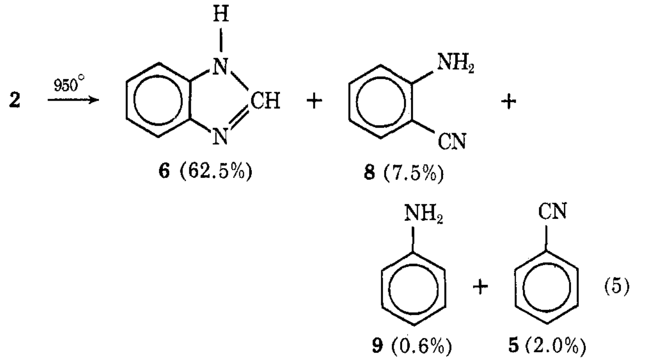
[10] E. K. Fields and S. Meyerson, *Int. J. Sulfur Chem., Part C*, **6**, 51 (1971).

Scheme II



Other prominent ions are *m/e* 92 and 91, which correspond to ions in the mass spectrum of aniline, and *m/e* 123, formed by the loss of HCN from the molecular ions. At 15 eV, the intensities are *m/e* 150 (100), 123 (3), 118 (9.5) and 92 (2.0); and at 12 eV they are *m/e* 150 (100) and 118 (8.0). The C_6H_5N ion at *m/e* 91 could have the structure of the molecular ions of cyanocyclopentadiene (**7**).

Benzimidazole-2-thione (**2**) was pyrolyzed at various temperatures between 850 and 1000°. The products and percentages obtained at 950° are given in eq 5.



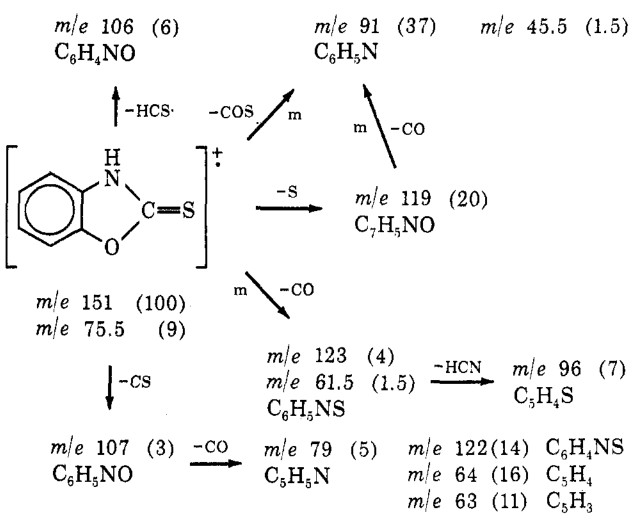
No starting material was recovered at 850° or above. Benzimidazole (**6**) and 2-cyanoaniline (**8**), the major products, are isomers and account for 70% of the starting material. The yield of **6** is at a maximum at 950° and decreases to 27% at 1000°, whereas the yield of **8** increases to 13% at 1000°.

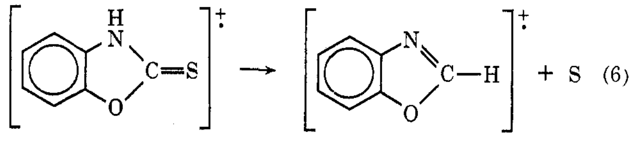
Benzimidazole (**6**) was pyrolyzed at 900 and 1000° under the same conditions as used in the pyrolyses of **2**. At 900°, 91% of **6** was recovered and 2.6% of **8** was isolated. At 1000°, the yields were 83.6 and 13.8%, respectively. At 1000°, the pyrolysis of **8** gave 1.5% of aniline (**9**) and 71.6% of recovered **8**. Therefore, **8** is formed from **6** as the result of a secondary pyrolysis, and **9** is formed from **8**. The small amount of **5** probably comes from a higher energy path.

Thus, the major products in the pyrolysis and the major fragmentation in the mass spectrum result from initial elimination of S.

Benzoxazole-2-thione (3).—The 70-eV mass spectrum of benzoxazole-2-thione (**3**) is given in Figure 1 and is summarized in Scheme III. At 8 eV, the paths involving the initial loss of S and COS are the only ones remaining: *m/e* 151 (100), 119 (25), and 91 (11). Other fragmentations at 70 eV of the molecular ions commence with initial losses of neutral molecules and radicals such as CO and CS. The ions formed from *m/e* 151 by loss of S can be visualized as the molecular ions of benzoxazole (**10**) (eq 6).

Scheme III

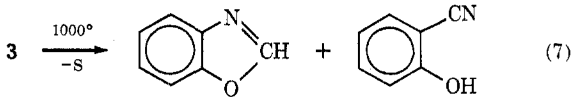




m/e 151 *m/e* 119

In the chemical ionization mass spectrum of **3**, there is no evidence of the loss of COS from the (M + H) ions. The peak at *m/e* 120 (M + H − S) is 6% of the intensity of *m/e* 152 (M + H). There are no other prominent fragments of the (M + H) ion.

Pyrolysis of **3** is first observed, under our conditions, at 850° and no starting material is recovered above 950°. At 1000°, benzoxazole (**10**, 1.3%) and its isomer 2-cyanophenol (**11**, 37.7%) account for 39% of the starting material (eq 7), resulting from the initial loss of S. The pyrolyses of **10** and **11** were also performed in this study, at 900 and 1000°. Benzoxazole (**10**) is converted to **11** in 82% yield at 900°. It is interesting to note that **11** irreversibly cyclizes to **10** upon photolysis.[11]



10 (1.3%) **11** (37.7%)

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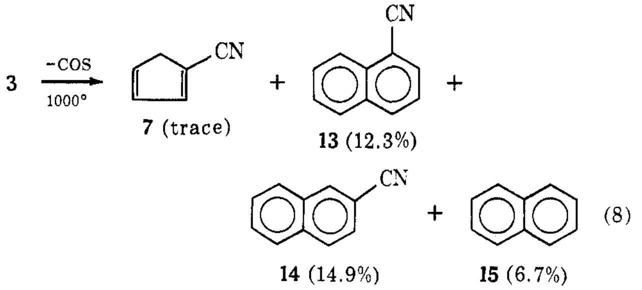
[11] J. P. Ferris and F. R. Antonucci, *Chem. Commun.*, 126 (1972).

Aniline (**9**, 3.2%), cyanobenzene (**5**, 2.0%), and phenol (**12**, 3.2%) are also isolated at 1000° from **3**. At 1000°, a small amount of phenol is formed from **10**; also phenol and cyanobenzene are formed from **11** when it is pyrolyzed at 900–1000°, in small yields.

Another series of products is observed from **3**. They are probably related to one another because they are not formed when CH_3OH is added to the stream, although **10**, **11**, **9**, **5**, and **12** still are. These compounds are cyanocyclopentadiene (**7**, trace), 1-cyanonaphthalene (**13**, 12.3%), 2-cyanonaphthalene (**14**, 14.9%), and naphthalene (**15**, 6.7%), eq 8. The origin of these products is being studied in detail and will be the subject of another report. The products are best explained by a loss of COS from **3** (eq 8) competing with the loss of S (eq 7).



(8)

The products shown in eq 7 and 8 account for 81.3% of the starting material, assuming that two molecules of **3** are necessary to form one molecule of **13–15**. Thus two main processes are taking place when benzoxazole-2-thione (**3**) is pyrolyzed: the initial loss of S and the initial loss of COS. If the yields of the products associated with the initial loss of S are added together and those associated with the initial loss of COS are added, the ratio of path S to path COS is 4 at 850° and 1.1 at 1000°. As the temperature increases, the loss of COS competes more successfully with the loss of S.

At 10 eV the ratio of the relative intensities of m/e 119 (M − S) and m/e 91 (M − COS) is 1.1; at 7 eV, it is 4.7. Eventually, m/e 91 disappears and only m/e 119 remains, along with the molecular ion. Thus both at the lower voltages and the lower pyrolysis temperatures, the initial loss of S predominates.

Conclusions

The pyrolytic and electron-impact fragmentations of the thiones **1–3** are similar, showing that the lowest energy paths in the mass spectra can be compared with the lowest energy pyrolytic paths. In these molecules, there are no alkyl groups or other substituents which would give stable ions having no equivalent in pyrolysis. Thus, the mass-spectral fragmentations seem to be governed by the elimination of small, neutral species rather than by the stability of the charged species. Also, the pyrolytic fragmentations are driven by the elimination of the same molecules.

In summary, in their low-energy paths, **1** and its molecular ions eliminate S and S_2; **2** and its molecular ions eliminate S; and **3** and its molecular ions eliminate S and COS. Always, the loss of S is the lower energy process; it is the only path observed from the (M + H) ions upon chemical ionization. Yields are relatively high from the pyrolyses, ranging from 40 to 80% under conditions which do not give any recovered starting material. Since all the products which were isolated are known compounds, these pyrolyses are not obviously useful from a synthetic standpoint. The interesting aspects of this work are the parallels observed between the mass-spectral and pyrolytic fragmentations.

Experimental Section

Melting points were determined by the open capillary method with a Thomas-Hoover or a Mel-Temp melting point apparatus and were corrected. Infrared spectra were recorded with a Perkin-Elmer Infracord or Beckman IR-8 spectrometer. Ultraviolet spectra (1 cm path) were determined on a Bausch and Lamb Spectronic 505. Nmr spectra were taken on a Varian T-60 or a JEOLCO A-60 spectrometer using 1% TMS as an internal standard. Low-resolution mass spectra were obtained from AEI-MS 902, Hitachi RMU-6D, and LKB 9000 mass spectrometers. Electron voltage readings were taken directly from the dial, since more precise values were not needed. Exact-mass measurements were obtained from an AEI-MS 902 mass spectrometer equipped with a PDP-8 computer. For 72.2% of the peaks studied, the deviations between the calculated and experimental masses were $\leq \pm 0.001$ mass units (mu). For 25.0% of the peaks studied, the deviations were 0.003–0.001 mu; and for 2.8% of the peaks, the deviations were 0.005–0.003 mu. Metastable peaks were observed in the low-resolution spectra, and, in addition, some metastable transitions were studied with the MS 902 while scanning in the defocused metastable mode.

The chemical ionization mass spectra were obtained from an AEI-MS 902 mass spectrometer, using isobutane. A source temperature of 250° and a probe temperature of 70–80° were used.

The glpc work was carried out using a Hewlett-Packard 5752B research chromatograph with a thermal conductivity detector. Columns were prepared with 0.25 in. copper tubing and 60/80 mesh Chromosorb W as a solid support, unless otherwise stated. A total of 17 columns was used; during the initial stages of analysis of the pyrolysis mixtures, most of the columns were tried. However, only the column that gives the best separations is reported in the Experimental Section. Comparison of the areas under the peaks of the pyrolysis products with the areas under peaks of solutions of known concentrations of the same compound was used to determine yields.

Chemicals.—Benzothiazole-2-thione (**1**) and benzimidazole-2-thione (**2**) were obtained from Aldrich Chemical Co., and benzoxazole-2-thione (**3**) was obtained from Eastman Organic Chemicals. Compounds **1–3** were recrystallized prior to use, and their purities were further checked by glpc, tlc, and mass spectrometry: **1**, mp 180–181° (lit.[12] mp 178–180°); **2**, mp 299–301° (lit.[13] mp 303–304°); and **3**, mp 194–195° (lit.[13] mp 193–195°).

Benzothiazole (**4**), 2-cyanoaniline (**8**), benzoxazole (**10**), and 2-cyanophenol (**11**) were purchased from the Aldrich Chemical Co. Benzimidazole (**6**) and 1- and 2-cyanonaphthalene (**13** and **14**) were purchased from Eastman Organic Chemicals.

Pyrolysis Apparatus.—Dry N_2 was passed through a tube fitted with a fritted disc on which were placed solid samples. The N_2 flow rate was monitored and controlled with a rotometer which was placed before the sample holder. Heating tape wrapped around the outside of the sample holder was used to sublime the sample into the pyrolysis tube. An auxiliary inlet was connected to a round-bottomed flask from which liquid samples were distilled into the pyrolysis tube; this inlet was also used to introduce a trapping agent (*e.g.*, CH_3OH) into the pyrolysis zone. Thus, the sample, N_2, and the trapping agent can pass through the pyrolysis zone simultaneously (trapping method A).

The sample holder was connected to a 24 × 1 in. (i.d.) hollow quartz pyrolysis tube. A 12-in. Hoskin electric furnace surrounded the quartz tube. The temperature of the furnace was controlled and read on a Thermolyne Corp. Temcometer. The temperature reported is approximately that of the internal portion of the quartz tube in the center of the oven.

A variety of traps was placed between the quartz tube and a vacuum pump. These traps were cooled by air and/or liquid N_2. Sometimes, the pyrolysis products were condensed on a cold

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[12] D. J. Banks and P. Wiseman, *Tetrahedron*, **24**, 6791 (1968).

[13] J. A. VanAllen and B. D. Deacon, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 569.

finger (Dry Ice–2-propanol) on which a trapping agent (*e.g.*, CH_3OH) was refluxing (trapping method B). A manometer and a McLeod gauge placed before the pump were used to read the pressure of the system.

Pyrolysis Procedure.—In a typical experiment approximately 2 g of sample was placed on the fritted disc (for solid samples) or in the round-bottomed flask (for liquid samples). Then the pyrolysis system was evacuated and flushed with dry N_2. After a few minutes the N_2 flow was adjusted to the desired rate. The electric furnace was then brought to temperature while the coolants were added to the dewar flasks surrounding the traps. The sample was sublimed or distilled through the pyrolysis tube. Upon completion of the pyrolysis, the oven was turned off and the quartz tube was allowed to cool to about 200°. Then dry N_2 was used to bring the system to atmospheric pressure and a solution was made of the material in the traps. This solution was worked up using glpc and tlc.

Pyrolysis of Benzothiazole-2-thione (**1**).—The conditions used in the pyrolyses of benzothiazole-2-thione (**1**) and the results are summarized in Table I. In each case, three traps were employed; the first was air cooled and the next two were cooled with liquid N_2. The products were identified as benzonitrile (**5**) and benzothiazole (**4**) by comparison of their retention times and their ir and mass spectra with those of commercial compounds. A 6-ft 20% SE-30 column, programmed between 50 and 260° at 10°/min, was used to analyze the pyrolysis mixtures.

TABLE I

CONDITIONS[a] USED IN THE PYROLYSIS OF BENZOTHIAZOLE-2-THIONE (1) AND RESULTS

Quantity, g	Temp, °C	1, % recovd	4, %	5, %	Total, %
1.141	700	31.6	8.4	0.8	40.6
1.500	750	16.7	17.1	4.6	38.4
1.210	800	0.0	23.1	13.1	36.2
1.410	850	0.0	16.3	24.3	40.6
1.288	900	0.0	6.6	34.1	40.7
1.199	950	0.0	0.0	44.4	44.4

[a] A N_2 flow rate of 0.20–0.28 l./min and a system pressure of 2.10–2.75 Torr were used.

Pyrolysis of Benzothiazole (**4**).—The conditions used and yields from the pyrolyses of benzothiazole (**4**) are summarized in Table II.

TABLE II

CONDITIONS[a] USED IN THE PYROLYSIS OF BENZOTHIAZOLE (4) AND RESULTS

Quantity, g	Temp, °C	4, % recovd	5, %	Total, %
1.36	750	64.4	0.6	65.0
1.600	800	49.0	3.0	52.0
1.438	850	26.8	11.2	38.0
1.778	900	12.8	32.0	44.8
1.376	950	6.9	44.2	51.1

[a] A N_2 flow rate of 0.20–0.22 l./min and a system pressure of 2.0–3.5 Torr were used.

The sample was distilled into the pyrolysis zone from a 25-ml round-bottomed flask. One air-cooled and two liquid N_2 cooled traps were used. Glpc, with a 20% SE-30 column, was used to analyze chloroform solutions of the pyrolysis products. The temperature rise was programmed between 50 and 260° at 15°/min. Benzonitrile (**5**) was the only major product, other than recovered starting material.

Pyrolysis of Benzimidazole-2-thione (**2**).—The conditions used for the pyrolyses of benzimidazole-2-thione (**2**) and the results are summarized in Table III.

The pyrolysis products were eluted with methanol and chloroform from the air-cooled and the two liquid N_2 cooled traps. Then the solutions were analyzed with a 6-ft 10% Carbowax 20M column programmed at 50–250° at 15°/min, by thin layer chromatography, and/or by the LKB-9000 gc/mass spectrum combination using a 6-ft 3% OV-1 CHROM HP 80/100 mesh column, isothermal at 110°.

TABLE III

CONDITIONS[a] USED IN THE PYROLYSES OF BENZIMIDAZOLE-2-THIONE (3) AND RESULTS

Quantity, g	Temp, °C	5, %	9, %	8, %	6, %	Total, %
1.483	850	2.0	0.2	4.7	55.8	62.7
1.302	900	2.6	0.6	7.5	61.1	71.8
1.671	950	2.0	0.6	7.5	62.5	72.6
1.451	1000	1.1	2.1	13.0	26.6	42.8

[a] A N_2 flow rate of 0.20–0.22 l./min and a system pressure of 2–5 Torr were used.

Aniline (**9**), benzonitrile (**5**), 2-cyanoaniline (**8**), and benzimidazole (**6**) were identified by comparison of the products with commercial samples.

Pyrolysis of Benzimidazole (**6**).—The conditions used for the pyrolyses of benzimidazole and the results are given in Table IV.

TABLE IV

CONDITIONS[a] USED IN THE PYROLYSES OF BENZIMIDAZOLE (6) AND RESULTS

Quantity, g	Temp, °C	6, % recovd	8, %	Total, %
1.424	900	91.3	2.6	93.9
1.613	1000	83.6	13.8	97.4

[a] A N_2 flow rate of 0.22 l./min and a system pressure of 2–5 Torr were used.

The pyrolysis mixtures were analyzed with a 10% QF-1 column, programmed at 150–230° at 15°/min; the temperature was then held at 230° for 5 min. The presence of 2-cyanoaniline (**8**) and starting material was detected.

Pyrolysis of 2-Cyanoaniline (**8**).—At 1000°, 1.552 g of 2-cyanoaniline (**8**) (N_2 flow rate 0.22 l./min at 3 Torr) was pyrolyzed. The traps were eluted with methanol and chloroform. The resulting dark brown solution was analyzed using the same chromatographic column (10% QF-1) and conditions as in the previous pyrolysis. Using retention times and areas under the peaks (by weighing), it was determined that 1.5% of aniline (**9**) and 71.6% of starting material (**8**) were in the traps.

Pyrolysis of Benzoxazole-2-thione (**3**).—The pyrolyses of benzoxazole-2-thione (**3**) were performed under the conditions described in Table V along with the results. The pyrolysis products were washed from the traps with methanol, acetone, and chloroform to give a total volume of approximately 300 ml. Then, most of the solvent was removed under vacuum to give 20–30 ml of solution, which was analyzed chromatographically. Two glpc columns were used. The first column (6-ft 10% Carbowax 20M) was programmed at 150-230° at 15°/min and was then held at 230° for 10 min. Under these conditions, six major components were separated.

The second column (6-ft 3% OV-1 CHROM HP 80/100 mesh) was programmed at 90–200° at 6°/min and revealed a seventh component. Its mass spectrum has peaks at *m/e* 128 ($M\cdot^+$), 127, 102, 64, 51, and 39. There also is a metastable peak at *m/e* 82.5 which corresponds to the loss of C_2H_2 from the molecular ion. It has the same retention time as naphthalene and was enhanced upon addition of naphthalene to the pyrolysis mixture.

At 1000°, no more starting material was present in the mixture of products but a new compound was detected when both columns were used. This product was determined to be benzonitrile (**5**) by its glpc characteristics and its smell.

A very minor component was detected when gc/mass spectrum was employed. Its molecular ion was found at *m/e* 91 and loses 27 mass units to give an ion at *m/e* 64. The structure of this component is tentatively assigned as 1-cyanocyclopentadiene (**7**).

The rest of the products were identified by comparison of their retention times, ir, uv, and mass spectra, and, in the case of **11**, melting point, with those of commercial samples.

Pyrolysis of Benzoxazole (**10**).—Conditions for the pyrolyses of benzoxazole (**10**) and results are given in Table VI. The traps

TABLE V

CONDITIONS[a] USED IN THE PYROLYSES OF BENZOXAZOLE-2-THIONE (3) AND RESULTS

Quantity, g	Temp, °C	3, % recovd	10, %	9, %	12, %	13, %	14, %	11, %	15, %	5, %	Total, %
1.854	850	59.9	1.3	0.2	2.0	0.9	1.0	8.6	0.9	0	74.8
1.620	900	33.9	1.3	1.3	4.1	3.6	4.1	24.1	4.4	0	76.8
1.603	950	14.2	1.5	2.0	5.1	6.2	7.4	27.3	11.1	0	74.8
1.603	1000	0	1.3	3.2	3.2	12.3	14.9	37.7	6.7	2.0	81.3
1.914[b]	1000	0	1.2	1.7	1.8	8.2	12.8	24.3	0	0	50.0
1.769[c]	1050	0	3.6	4.7	5.2	0	0	55.7	0	0	69.2

[a] A N_2 flow rate of 0.20–0.22 l./min was used and a system pressure of 1–4 Torr was maintained. [b] CH_3OH was used as a trapping agent following method B. [c] CH_3OH was used as a trapping agent following method A.

TABLE VI

CONDITIONS[a] USED FOR THE PYROLYSES OF 10 AND RESULTS

Quantity, g	Temp, °C	10, % recovd	11, %	12, %	Total, %
1.960	900	4.0	81.6	0	85.6
1.728	1000	2.8	55.0	1.6	59.4

[a] A N_2 flow rate of 0.25 l./min and a system pressure of 1–2 Torr were used.

TABLE VII

CONDITIONS[a] USED IN THE PYROLYSES OF 11 AND RESULTS

Quantity, g	Temp, °C	11, % recovd	5, %	12, %	Total, %
1.464	900	74.1	1.5	0	75.6
1.498	1000	58.5	3.6	6.1	68.2
1.807[b]	1000	88.8	2.1	0	90.9

[a] A N_2 flow rate of 0.22 l./min and a system pressure of 1–3 Torr were used. [b] CH_3OH was used as a trapping agent *via* method B.

were eluted with a mixture of solvents, *ca.* 300 ml, and then the volume was reduced to 20–30 ml under vacuum. Gas chromatographic analyses using the same columns and the same programming used in the pyrolyses of **3** were used.

Pyrolysis of 2-Cyanophenol (11).—The conditions used in the pyrolyses of 2-cyanophenol (**11**) and the results are given in Table VII. The glpc work-up was the same as that used in the study of the pyrolyses of **3**. In addition to **5** and **12**, gc/mass spectrum revealed a minor amount of a component with a molecular ion at *m/e* 91 which loses 27 mu, probably cyanocyclopentadiene (**7**). A minor amount of toluene was also detected by the LKB 9000.

Registry No.—**1,** 4464-58-8; **2,** 2080-59-3; **3,** 14955-23-8; **4,** 95-16-9; **6,** 51-17-2; **8,** 1885-29-6; **10,** 273-53-0; **11,** 611-20-1.

Acknowledgments.—We wish to thank Dr. T. Chang of Wyeth Laboratories, Philadelphia, Pa., for the chemical ionization mass spectra of **1** and **3**. Also, we wish to thank Dr. O. A. Mamer, Royal Victoria Hospital, Montreal, for use of the LKB 9000 gc/mass spectrum combination. This investigation was supported by grants from the National Research Council of Canada and the National Institutes of Health (U. S.).

Reaction of 1,1-Dichloro-2-phenylsulfonylcyclopropanes with Sodium Alkoxides[1]

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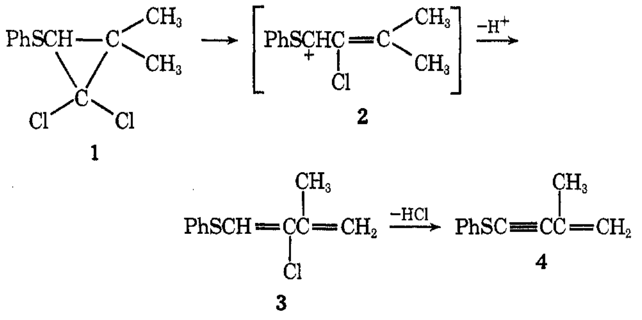
Received November 27, 1972

Reaction of 1,1-dichloro-2,2-dimethyl-3-phenylsulfonylcyclopropane (**5**) with sodium methoxide in methanol or sodium ethoxide in ethanol at room temperature gives excellent yields of the corresponding cyclopropyl ketals (**6a**, **6b**); the corresponding thioketal (**7**) is formed with thiophenoxide. The cyclopropyl ketals are unstable in hot alcohols and are converted quantitatively into ortho esters (**8a**, **8b**) or mixed ortho esters (**8c**). Reactions with two other analogous dihalocyclopropanes (**13**) are described; conversion to ortho esters proceeds generally and in high yield.

We have previously shown that 2,2-dichlorocyclopropyl phenyl sulfides of type **1** are unstable in hot alcohols, and in the presence of the strong base potassium *tert*-butoxide[3] give enynes (**4**) as illustrated for **1** in Scheme I. The accelerating effect of the sulfur atom is considered to be a driving force for this exocyclic ring opening reaction, since sulfur can stabilize the positive charge developed in the transition state (or intermediate **2**).

SCHEME I



Replacement of the phenylmercapto group in **1** by the phenylsulfonyl group (as in **5**) would destabilize an intermediate ion corresponding to **2**, and, as expected, dihalo-2-phenylsulfonylcyclopropanes have been found to be comparatively thermally stable. These sulfones do, however, react readily with alkoxides

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[1] Supported in part by National Science Foundation Grant GP-11918.

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[3] W. E. Parham, S. Kajigaeshi, and S. H. Groen, *Bull. Chem. Soc. Jap.*, **45**, 509 (1972).