# Pyrolyses and Mass Spectra of 2-Benzoxazolinone, 2-Benzimidazolinone, and 2-Benzothiazolinone

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The electron-impact and chemical-ionization mass spectra of 2-benzoxazolinone (5), 2-benzimidazolinone (6), and 2-benzothiazolinone (7) have been compared with their pyrolysis products and parallels have been found. In each case, loss of CO occurs from  $M^{\ddagger}$ , followed by loss of CO for 5 and by HCN for 6 and 7. At 950° in a stream of N<sub>2</sub>, 5 gave 17% of C<sub>5</sub>H<sub>5</sub>N isomers, related to the loss of 2CO, along with 5.6% of quinoline. Compound 6 gave 14% of C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> isomers, related to the loss of CO. At 950°, 7 gave 2-thiophenecarbonitrile (1.1%), cyanonaphthalenes (4.5%), aniline (3%), cyanobenzene (2.5%), naphthalene (1.5%), and phenylisocyanate (2.5%). From 5–7 20–70% of the starting material was recovered or accounted for by isolation and identification of products in each case. G.c./m.s. was used to study pyrolysis mixtures.

On rapporte les spectres de masse de la benzoxazolinone-2 (5), de la benzimidazolinone-2 (6) et de la benzothiazolinone-2 (7), tels qu'obtenus par impact électronique et par ionisation chimique en utilisant l'isobutane. On compare ces spectres avec les produits de pyrolyse des composés 5–7. Dans chaque cas, l'ion moléculaire élimine une molécule de CO. Pour les composés 6 et 7, ce processus est suivi d'une élimination de HCN, alors que pour le composé 5, il est suivi de la perte d'une deuxième molécule de CO. La pyrolyse du composé 5 à 950° dans un courant d'azote conduit à la formation de quinoline (5.6%) et d'isomères répondant à la formule  $C_5H_5N$ , ces derniers à la suite de l'élimination de deux molécules de CO. Parallèlement, le composé 6 donne des isomères répondant à la formule  $C_5H_4N_2$  par élimination d'une molécule de CO et d'une molécule de H<sub>2</sub>. Les produits de la pyrolyse du composé 7 à 950° sont le thiophènecarbonitrile-2 (1.1%), les cyanonaphthalènes (4.5%), l'aniline (3%), le cyanobenzène (2.5%), le naphthalène (1.5%) et l'isocyanate de phényle (2.5%). Les produits de group is produits originaux récupérés représentent de 20 à 70% des produits de départ. La combinaison de la chromatographie en phase gazeuse avec la spectrométrie de masse était employée pour étudier les mélanges obtenus des pyrolyses.

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#### Introduction

We have compared the electron-impact (e.i.) and chemical-ionization (c.i.) mass spectra of 2-benzothiazolinethione (1), 2-benzimidazolinethione (2), and 2-benzoxazolinethione (3) with their pyrolysis products, and parallels have been found (1). The loss of S from the molecular ions



is the lowest energy fragmentation observed at low voltages. Also, the loss of S is the only fragmentation observed from their (M + H) ions in the chemical-ionization mass spectra. The loss of

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S is also observed upon pyrolysis. For example, 2-benzothiazolinethione (1) gives a 23% yield of benzothiazole (4) and a 13% yield of cyanobenzene at 800°. The formation of 4 can be accounted for by the loss of S from 1; cyanobenzene forms by loss of  $S_2$  from the 2-thione and by loss of S from 4. This one-step loss of  $S_2$  is also observed in the mass spectrum of 1.

This study has now been extended to 2-benzoxazolinone (5), 2-benzimidazolinone (6), and 2-benzothiazolinone (7). U.v. and i.r. spectra indicate that 5 exists predominantly in the lac-



tam form (2), so we will use this structure in the schemes even though we don't know the structure of the molecular ions. Likewise, i.r. spectra and dipole moments provide evidence for the presence of the keto structure of 6, (3) and

measured  $^{14}$ N chemical shifts have shown that 7 exists exclusively in the thiazolinone form (4).

In each case, the 2-ones 5–7 have been pyrolyzed several times at a variety of temperatures. Their mass spectra have been obtained under conditions of electron impact (e.i.) at 70 and lower eV. Exact-mass measurements have been made in order to determine the elemental compositions of the ions. Also, the chemical ionization (c.i.) mass spectra have been obtained for comparison with the e.i. spectra and with the products of pyrolysis.

Millard and Temple have briefly described the e.i. mass spectrum of 2-benzothiazolinone (7) (5), and the e.i. mass spectrum of 2-benzoxazolinone (5) has been reported but not discussed (6). The 70 eV e.i. mass spectrum of 2-benzimidazolinone (6) is given in Fig. 1. Even though the mass spectrum of 6 has not been published, the e.i. mass spectra of 11 substituted 2-benzimidazolinones have been studied (7).

Our samples were pyrolyzed by sublimation into a stream of  $N_2$  which passed through a hollow quartz tube surrounded by a 12 in. furnace (1,8). In general, a  $N_2$  flow rate of 0.25 l/min and a system pressure of 2.5 Torr were used. Pyrolysis products have been identified by isolation and characterization. Combined gas chromatography – mass spectrometry (g.c.-m.s.) was also used.

## Experimental

Melting points were determined by the open capillary method using a Mel-Temp apparatus and were corrected.



#### MASS-TO-CHARGE RATIO

FIG. 1. The e.i. mass spectrum (70 eV) of 2-benzimidazolinone. I.r. spectra were recorded with a Beckman IR8 and a Perkin-Elmer Infracord. N.m.r. spectra were taken on a Varian T-60 spectrometer using 1% TMS as an internal standard. U.v. spectra (1 cm path) were determined on a Bausch and Lomb Spectronic 505. Low resolution mass spectra were obtained from a Hitachi RMU-6D mass spectrometer. Electron voltage readings were taken directly from the dial since more precise values were not needed. Combined g.c.-m.s. data were determined with a LKB 9000 instrument.

Exact-mass data were obtained from an AEI MS 902 mass spectrometer linked to a PDP 8 computer. All experimental values agreed with the calculated values within  $\pm 0.0015$  mass units. The c.i. mass spectra were taken from a Dupont 21/491 mass spectrometer at a source temperature of 250° and a probe temperature of 80°, using isobutane.

The g.l.p.c. 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 13 columns was used; during the initial stages of analysis of the pyrolysis mixtures most of the columns were tried. However, only the column that gave the best separations is reported for each analysis. Comparison of the areas under the peaks of the pyrolysis products with the areas under the peaks of solutions of known concentrations of the same compound was used to determine yields.

#### Chemicals

2-Benzoxazolinone (5) was purchased from Eastman Organic Chemicals, m.p. 138–139° (lit. (9) m.p., 137–138°). 2-Benzimidazolinone (6) was obtained from Aldrich Chemical Co., m.p. 316–317° (lit. (10) m.p., 313–316°). Their purities were also checked by g.l.p.c., t.l.c., and mass spectrometry. 2-Cyanoaniline, 2-cyanopyridine, 3-cyanopyridine, and 4-cyanopyridine were also purchased from Aldrich. 1- and 2-cyanonaphthalene were purchased from Eastman.

#### 2-Benzothiazolinone (7)

2-Benzothiazolinone (7) was prepared from 2-benzothiazolinethione (1) by the procedure of Efros and Davidenkov (11). Yield 6.5 g (36%), m.p.  $136-137^{\circ}$  (lit. (11) m.p.  $136^{\circ}$ ), i.r. (HCCl<sub>3</sub>) 3350 and 1675 cm<sup>-1</sup>.

Anal. Calcd. for  $C_7H_5NOS$ : C, 55.63; H, 3.31. Found: C, 55.77; H, 3.40.

#### cis, cis-2,4-Hexadienedinitrile

A mixture of *o*-phenylenediamine (2.4 g, Aldrich), lead tetraacetate (27.9 g), and 130 ml of ether was stirred under N<sub>2</sub> for 3 h. The solution turned dark brown, was filtered and washed with aqueous NaHCO<sub>3</sub> until neutral, and then washed with water. The ether layer was dried (MgSO<sub>4</sub>) and evaporated under vacuum. The brown residue was sublimed at 66°, 0.5 Torr, giving a white solid, m.p. 124-126° (lit. (12) m.p. 128-129°). G.l.p.c. traces and u.v. spectra showed no trace of the diamine.

# Pyrolysis Apparatus and Procedure

The pyrolysis apparatus and procedure have been described previously (1). The sample in a stream of nitrogen passes through a quartz tube heated by an electric furnace 12 in. long. The flow rate is 0.25 l/min at 2.5 Torr. A series of traps is placed between the quartz

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TABLE 1. Temperatures used in the pyrolyses of 2-benzoxazolinone (5) and results<sup>4</sup>

| Quantity (g)<br>and temperature<br>(°) | % recovered |     |      |     |     |     |     |     |                    |
|--|-------------|-----|------|-----|-----|-----|-----|-----|--------------------|
|  | 5           | 8   | 9    | 10  | 11  | 12  | 13  | 14  | Total <sup>ø</sup> |
| 1.933<br>900                           | 9.0         | 3.5 | 6.2  | 5.5 | 3.4 | 2.1 | 0.7 | 2.5 | 32.9               |
|  |             |     | 15.2 |     |     |     |     |     |                    |
| 1.733<br>950                           | 2.9         | 3.5 | 7.0  | 6.3 | 5.6 | 2.8 | 0.7 | 1.6 | 30.4               |
|  |             |     | 16.8 |     |     |     |     |     |                    |
| 1.444<br>1000                          | 0.0         | 2.4 | 5.6  | 5.1 | 3.6 | 2.0 | 0.1 | 1.4 | 20.2               |
|  |             |     | 13.1 |     |     |     |     |     |                    |

<sup>a</sup>Compounds 8–10 are isomeric; product 8 is pyridine; 9 and 10 are *cis* and *trans* isomers of 2,4-pentadieneni-trile; 11 is quinoline; 12 is cyanobenzene; 13 is aniline; and 14 is phenol. <sup>b</sup>It was assumed that one molecule of 5 is needed to produce one molecule of all products except 11, in which case two molecules of 5 are needed.

tube and the pump. A solution is made of the material in the traps. G.I.p.c. and t.I.c. are used to separate the compounds in this solution.

#### Pyrolysis of 2-Benzoxazolinone (5)

The temperatures used in the pyrolyses of 2-benzoxazolinone (5) and the results are summarized in Table 1. A N<sub>2</sub> flow rate of 0.25 l/min was used. The initial pressure of the system was 0.8-1.2 Torr; it increased to a maximum of 6.0 Torr as 5 was sublimed into the N<sub>2</sub> stream and returned to its original value when all starting material had passed through. The products were collected in three traps, each cooled with liquid nitrogen. These traps were eluted with CH3OH, acetone, and CHCl3, and the combined washings were analyzed by g.l.p.c. The best separation of lower molecular weight components was achieved with a 12 ft 10% Carbowax 20M column held at 100° for 10 min, then programmed to 230° at 8°/min, and then held at 230° for 10 min. The other components were studied with a 6 ft 3% OV-225 CHROM HP 80/100 mesh column held at 100° for 2 min, then programmed to 250° at 8°/min, and then held at 250° for 4 min.

The mass spectra of products 8-10 show molecular-ion peaks at m/e 79 and a loss of HCN, giving m/e 52. Product 8 was identified as pyridine by comparison of its u.v. spectrum and g.l.p.c. retention time with those of a commercial sample. Products 9 and 10 were identified as the cis and trans isomers of 2,4-pentadienenitrile on the basis of their mass, n.m.r., i.r., and u.v. spectra. For example, absorption at  $2220 \text{ cm}^{-1}$  is characteristic of the cyano group; also, absorptions at 1570 and 665 cm<sup>-1</sup> are characteristic of the cis form whereas 1592 and 950 cm<sup>-1</sup> are characteristic of the trans form (13). It is interesting to note that approximately equal amounts of the two isomers were formed via equilibration at 575° of the cis form to the cis, trans mixture (14). We also obtain nearly equal amounts of each isomer.

Product 11 was shown to be quinoline on the basis of its u.v. spectrum and retention time, compared to those of a commercial sample. Likewise, product 12 was found to be cyanobenzene; 13 was found to be aniline; and 14

was found to be phenol by comparison of their retention times and spectra with those of commercial samples.

### Pyrolysis of 2-Benzimidazolinone (6)

The temperatures used in the pyrolyses of 2-benzimidazolinone (6) and the results are given in Table 2. A flow of  $N_2$  of 0.23 l/min and a system pressure of 1-3 Torr were used. The air-cooled trap and the two liquid nitrogen-cooled traps were eluted with EtOH, MeOH, acetone, and CH<sub>2</sub>Cl<sub>2</sub>. The solutions were combined and concentrated.

Mass spectra of the products were obtained from a LKB 9000 g.c.-m.s. combination using a 6 ft 3% OV-210 CHROM HP 80/100 mesh column programmed between 100 and 200° at 4°/min. The products were collected from a 6 ft 10% QF-1 CHROM HP 80/100 mesh column programmed in the same manner. Since starting material (6) does not elute from either column, it was recovered from a 6 ft 3% OV-1 CHROM HP 80/100 mesh column programmed between 100 and 250° at 15°/min and then held at 250° for 5 min.

Products 15-20 are isomeric; their mass spectra contain molecular ions at m/e 104 and intense fragment peaks at m/e 77. Compounds 15–17 are the isometric cyanopyridines and 18-20 are the isomeric 2,4-hexadienedinitriles. 2-Cyanopyridine (15) and its 3-cyano (16) and 4-cyano (17) isomers and 2-aminocyanobenzene (21) were identified by g.l.p.c. retention times compared with those of commercial samples, g.l.p.c. peak enhancement, and comparison of their mass, i.r., and u.v. spectra with those of the known materials. The product cis, cis-2, 4-hexadienedinitrile (18) was identified by retention time, peak enhancement, and mass and u.v. spectra, compared with the sample prepared as described above. Aniline (13) and cyanobenzene (12) were likewise characterized by comparison.

The three hexadienedinitriles gave identical mass spectra and very similar u.v. spectra with maxima at 261 nm. All three have been reported to have maxima near 260 nm (15). The cis, cis isomer (18) was identified on the g.l.p.c. trace by comparison and peak enhancement. For the two remaining isomeric hexadienedinitriles,

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|                                       | % recovered                    |   |   |  |     |     |     |       |  |
|---------------------------------------|--------------------------------|---|---|--|-----|-----|-----|-------|--|
| Quantity (g)<br>nd temperature<br>(°) | Cyano-<br>pyridines<br>6 15-17 |   | Hexadienedinitriles<br>18–20              |  |     | 13  | 12  | Total |  |
| 2.259<br>950                          | 56.5                           | 2-, 2.3<br>3-, 3.0<br>4-, 1.3<br><u>6.6</u> | cis,cis-,<br>cis,trans-,<br>trans,trans-, | $   \begin{array}{r}     0.7 \\     1.1 \\     0.4 \\     \hline     2.2   \end{array} $ | 0.4 | 2.3 | 0.8 | 68.8  |  |
|                                       |                                | 8.8 (0                                      | $C_6H_4N_2$                               |  |     |     |     |       |  |
| 2.572<br>1000                         | 10.2                           | 2-, 3.9<br>3-, 4.6<br>4-, 1.8               | cis,cis-,<br>cis,trans-,<br>trans,trans-, | 1.0<br>1.8<br>0.8  | 2.0 | 1.5 | 2.1 | 29.7  |  |
|                                       |                                | 10.3  |   | 3.6  |     |     |     |       |  |
|                                       |                                | 13.9 (0                                     | $C_6H_4N_2$                               |  |     |     |     |       |  |

# TABLE 2. Temperatures used in the pyrolyses of 2-benzimidazolinone (6) and results<sup>a</sup>

"Compound 21 is 2-aminocyanobenzene, 13 is aniline, and 12 is cyanobenzene.

TABLE 3. Temperatures used in the pyrolyses of 2-benzothiazolinone (7) and results<sup>a</sup>

| Quantity (g)<br>and temperature<br>(°) | % recovered |     |     |     |     |     |     |     |     |       |
|--|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-------|
|  | 7           | 25  | 23  |     | 24  | 12  | 13  | 22  | 26  | Total |
| 2.959<br>950                           | 8.7         | 1.1 | 2.4 | 4.2 | 1.8 | 2.6 | 2.7 | 1.3 | 2.5 | 23.1  |
| 2.605<br>1000                          | 1.3         | 1.4 | 2.4 | 6.4 | 4.0 | 5.4 | 1.8 | 1.7 | 3.7 | 21.7  |

<sup>a</sup>Compound 25 is 2-thiophenecarbonitrile; 23 and 24 are 1- and 2-cyanonaphthalene; 12 is cyanobenzene; 13 is aniline; 22 is naphthalene; and 26 is methyl carbanilate.

the one which eluted first was assigned the cis, trans structure (19) and the other one, the *trans, trans* structure (20). Our experience with the isomeric 2,4-pentadienenitriles (9 and 10) showed that the *cis* isomer (9) eluted before the *trans* isomer (10).

### Pyrolysis of 2-Benzothiazolinone (7)

The temperatures used in the pyrolyses of 2-benzothiazolinone (7) and the results obtained are given in Table 3. A N<sub>2</sub> flow rate of 0.25 l/min was used, and the system pressure varied between 1.5 and 3.0 Torr during the pyrolyses. The traps were eluted with methanol, acetone, and  $CH_2Cl_2$ ; the solutions were combined, concentrated, and analyzed. The 6 ft 3% OV-210 CHROM HP 80/100 mesh column was held at 100° for 4 min, and then programmed to 200° at 4°/min. After reaching 200°, the oven was held there for 10 min.

Cyanobenzene (12), aniline (13), naphthalene (22), 1and 2-cyanonaphthalene (23 and 24), and starting material (7) were identified by comparison of their retention times and u.v. and mass spectra with those of commercial samples, and by g.l.p.c. peak enhancement. Product **25** was identified as 2-thiophenecarbonitrile on the basis of its mass (M<sup>+</sup>, m/e 109), i.r. (2250 cm<sup>-1</sup>), and u.v. ( $\lambda_{max}$  in CH<sub>2</sub>Cl<sub>2</sub>, 241.5 nm) spectra. The u.v. spectrum of 2-thiophenecarbonitrile has been observed at  $\lambda_{max}$  242 nm (16) whereas the 3-isomer absorbs at  $\lambda_{max}$  236 nm (17).

Another product (26) was identified as methyl carbanilate by comparison of its u.v., i.r., and mass spectra with those of a sample prepared by addition of phenylisocyanate to methanol.

## Discussion

# 2-Benzoxazolinone (5)

The 70 eV e.i. mass spectrum of 2-benzoxazolinone (5) is summarized in Scheme 1. Intense metastable peaks are found for losses of  $CO_2$  and 2CO from the molecular ions. The loss of CO from the molecular ions, followed by CO, is also observed in the metastable peaks, al-

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## SCHEME 2

though the metastable peak for the loss of 2CO is much more intense. The width and shape of the small metastable peak for the loss of CO indicates that internal energy is being released as translational energy of the fragments. For a discussion of the significance of the shapes of metastable peaks see ref. 18. At 15 eV, m/e 91

and 79 are approximately equally abundant,  $\sim 2\%$ . The (M + H) ion is present in the c.i. mass spectrum but there are no appreciable fragment ions present.

One can attempt to rationalize these data as shown in Scheme 2, as well as with other speculative ion structures. The loss of 2CO from the open-chain ion would require the two molecules to be lost from opposite ends of the chain. Previously, examples have been cited where a loss of two molecules from different parts of an ion

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<sup>&</sup>lt;sup>2</sup>The elemental compositions are the result of the exactmass measurements; the values in parentheses are relative intensities;  $m^*$  denotes a metastable peak found in the mass spectrum.

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gives rise to a metastable peak for the combined loss (Scheme 1, ref. 19). In comparison, the low energy fragmentations of the molecular ions of 2-benzoxazolinethione (3) are losses of S and COS (1). The only fragmentation in the c.i. spectrum of 3 is loss of S from the (M + H)ions (1).

The major products in the pyrolyses of 5 are three  $C_5H_5N$  isomers. When 1.9 g of 5 was pyrolyzed at 950° with a N<sub>2</sub> flow rate of 0.23 l/min and an initial system pressure of 0.8 Torr, 2.9% of 5 was recovered and 16.8% of  $C_5H_5N$ (8-10) was isolated, as shown in eq. 1.

Other products isolated were quinoline (11, 5.6%), cyanobenzene (2.8%), phenol (1.6%), and aniline (0.7%), for a total of 30.4% of the starting material accounted for. The formula of quinoline,  $C_9H_7N$ , corresponds to the dimerization of  $C_5H_5N$ , followed by loss of HCN and  $H_2$ .

Aniline could form by loss of  $CO_2$  from 5 followed by abstraction of 2H and phenol by loss of HNCO followed by addition of 2H. However, aniline, phenol, and/or cyanobenzene, which are common pyrolysis products from this type of heterocyclic compound (1), could form by a degradation-recombination mechanism.

If, indeed, 8-11 arise from  $C_5H_5N$  via initial loss of 2CO from the molecule, they, along with the 2.9% of recovered 5, account for 25.2 of the 30.4% of products isolated. Thus the major fragmentations observed in the mass spectrum of 5 can be used to rationalize the products formed upon pyrolysis.

### 2-Benzimidazolinone (6)

The 70 eV e.i. mass spectrum of 2-benzimidazolinone (6) is given in Fig. 1. In the c.i. spectrum of 6, the (M + H) ion at m/e 135 is present, but there are no abundant fragment ions. The major fragmentation pathway of 6 is the consecutive losses of CO and 2HCN, as summarized in Scheme 3. At 15 eV, the peaks which remain are m/e 134 (100), 106(5), and 105(3). The metastable peak for the loss of CO is broad and concave (18).

The structures given in eq. 2 can account for the major fragmentation path. In comparison, oxidation of 2-iminobenzotriazole (27) with lead tetraacetate gives 2,4-hexadienedinitrile in good yield (eq. 3) (20). The intermediate in brackets in eq. 3 could not be trapped with acetylene dicarboxylate. Also, the decomposition of aromatic o-diazides at  $160-170^{\circ}$  to 2,4-hexadienedinitriles via the same intermediate seems to be a general reaction (21).

At 1000°, we recovered 10.2% of the starting material (6), and we isolated 13.9% of  $C_6H_4N_2$  isomers, as shown in eq. 4. In addition, 2.0% of 2-aminocyanobenzene, 2.1% of cyanobenzene, and 1.5% of aniline were isolated. Thus, in all, 29.7% of the starting material has been accounted for. The percentages of the isomeric



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[1]

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 $[4] \qquad 6 \xrightarrow{-CO}_{1000^{\circ}} \left[ \underbrace{\swarrow NH}_{NH} \right] \xrightarrow{-H_2} \underbrace{\bigcirc N}_{N} CN + N \equiv C - (CH = CH)_2 - C \equiv N$   $\underbrace{15 - 17}_{10.3\%} \underbrace{18 - 20}_{3.6\%}$ 

[6]

cyanopyridines were 3.9% of the 2-isomer (15), 4.6% of the 3-isomer (16), and 1.8% of the 4-isomer (17). The 2,4-hexadienedinitriles were present as the *cis,cis* isomer (18, 1%), the *cis,trans* isomer (19, 1.8%) and the *trans,trans* isomer (20, 0.8%).

We have pyrolyzed benzimidazole (28) at  $1000^{\circ}$  and isolated 2-aminocyanobenzene (21), eq. 5 (1). It is possible that 6, in a high energy path, loses H<sub>2</sub>O or HO to give an intermediate,



similar to the intermediate from 28, which leads to formation of 21. The pyrolysis of 21 at  $1000^{\circ}$ gave aniline (1). Thus the formation of 21 and of aniline in the pyrolysis of 6 may be related.

Once again, the resemblance of the fragmentation in the e.i. mass spectrum to its pyrolytic paths is striking.

### 2-Benzothiazolinone (7)

In the c.i. mass spectrum of 2-benzothiazolinone (7), the (M + H) peak is present and there are no abundant fragment ions. In contrast, the peak for loss of S in the c.i. spectrum of the isomeric 2-benzoxazolinethione (3) is 6% of the intensity of the (M + H) peak (1).

In the 70 eV e.i. spectrum of 7 there is one major fragmentation path (eq. 6). As was the

$$\begin{array}{c}
H \\
N \\
\hline
N \\
\hline$$

$$m/e \ 123(40) \xrightarrow{\text{HCN}} m/e \ 96(41)$$
  
 $C_6H_5NS \qquad C_5H_4S$ 

case with the molecular ions of 5 and 6, the metastable peak for the loss of CO is broad and concave, indicating a release of internal energy. The peaks at m/e 123 and 96 persist as the electron voltage is lowered, with m/e 96 disappearing before m/e 123.

In the 70 eV e.i. mass spectrum of 3, the major fragmentations are losses of S and COS (1). However, there are small peaks at m/e 123(4%) for loss of CO and at m/e 96(7%) for loss of CO followed by HCN. Thus, it is possible that some of the molecular ions of 3 rearrange to the molecular ions of 7 before fragmenting. There are no substantial peaks at (M - S) or (M - S)

[2]

[3]

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COS) in the mass spectrum of 7. Dimethylthioncarbamates have been found to rearrange to dimethylthiolcarbamates upon heating and also upon electron impact (eq. 7) (22).

[7] 
$$A_r - O - C - N(CH_3)_2 \longrightarrow A_r - S - C - N(CH_3)_2$$

No products were isolated from the pyrolyses of 7 which could be directly related to the fragmentations in its mass spectrum. This is probably due to the fact that the sulfur atom is retained and gives products such as cyclopentadienethione ( $C_5H_4S$ ) which polymerize. At 950°, 8.7% of starting material was recovered and 14.4% of products was isolated and identified.

The major products are 1-cyanonaphthalene (23, 2.4%), 2-cyanonaphthalene (24, 1.8%), naphthalene (1.3%), aniline (2.7%), and cyanobenzene (2.6%). One can speculate that naphthalene and the cyanonaphthalenes are formed by the loss of COS and/or CO and S from 3 and 7, perhaps through the intermediacy of cyanocyclopentadiene (eq. 8). For example, dimerization

[8] 3 and 7 
$$\xrightarrow{1000^{\circ}}_{-\text{COS}}$$
  $\left[ \overbrace{C_6H_5N}^{\text{CN}} \right] \rightarrow 23 + 24$   
 $C_6H_5N$   $C_{11}H_7N$ 

of  $C_6H_5N$  gives  $C_{12}H_{10}N_2$  which can yield  $C_{11}H_7N$  (23 and 24) by losses of HCN and  $H_2$ , and naphthalene ( $C_{10}H_8$ ), by loss of 2HCN. We considered a similar possibility for the formation of quinoline from the pyrolysis of 5. Naphthalene (6.7%), 23 (12.3%), and 24 (14.9%) have also been obtained from the pyrolysis of 3, in addition to benzoxazole (4, O in place of S, 1.3%), and 2-cyanophenol (37.7%) (1). The possible intermediacy of cyanocyclopentadiene is being investigated.

Two other products were isolated in small yields at 950°, 2-thiophenecarbonitrile (25, 1.1%) and phenylisocyanate (29), isolated as its methyl carbanilate derivative (2.5%). Compound 29 can be formed from 7 by the loss of S and is trapped



by methanol when the traps which are cooled by liquid  $N_2$  are washed out after the pyrolysis is terminated. The origin of the small amount of 25 is more obscure. The overall yields obtained from the pyrolysis of the 2-ones 5–7 are substantially lower than the yields obtained from the corresponding 2-thiones 1-3 (1). The 2-thiones expel an atom of S, leaving a stable aromatic azole 30. On the other hand, the 2-ones expel CO, leaving an



30 X = S, NH, O 31 X = O, NH, S

ortho-quinoid intermediate (31), or a rearranged isomer which is unstable and polymerizes or degrades further.

Nevertheless, the  $C_5H_5N$  isomers (17% yield) and the quinoline (5.6% yield) obtained from the pyrolysis of 5 can be associated with the loss of CO from 31 (X = O). The loss of 2CO is also the major fragmentation in the mass spectrum of 5. Similarly, the formation of the  $C_6H_4N_2$ isomers (14% yield) from the pyrolysis of 6 can be associated with the loss of  $H_2$  from 31 (X = NH) and with the loss of CO from 6, followed by H, observed in the mass spectrum.

If compound 7 indeed forms 31 (X = S) upon pyrolysis, the loss of HCN would give  $C_5H_4S$ , cyclopentadienethione, which would not be expected to be stable and would polymerize. Loss of CS from 31 would give  $C_5H_5N$  which could react with S and lose H<sub>2</sub> to give thiophenecarbonitrile (25). On the other hand, loss of S from 31 (X = S) would give  $C_6H_5N$  which could lead to 23 and 24. The loss of CO followed by HCN is the major fragmentation observed in the mass spectrum of 7, whereas the loss of S from the (M - CO) ions is minor. It seems that the formation of 23 and 24 in the pyrolyses of 3 and 7 are likely related. In summary, the relationship between the pyrolysis and mass spectrum of 7 is ambiguous possibly because of the instability of sulfur containing products.

In conclusion, it has been possible to interpret the mass spectra and pyrolyses of 1–7 in terms of the extrusion of small species such as HCN, CO, and S, demonstrating another series of compounds which show similarity between the two processes. Upon pyrolysis, it is possible that major products do not survive to be isolated. If a large percentage of the starting material is not accounted for, this factor must be considered when the comparison is made between mass spectra and pyrolysis. If most of the starting material can be accounted for, on the other hand,

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it is evident that a major pyrolytic path has not been obscured.

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- 1. D. C. DEJONGH and M. L. THOMSON, J. Org. Chem. 38, 1356 (1973).
- N. L. ARYUTKINA, A. F. VASIL'EV, N. A. POZ-NANSKAYA, N. I. SHVETSOV-SHILOVSKII, S. N. IVANOVA, and N. N. MEL'NIKOV. Zh. Obshch. Khim. 40, 1872 (1970).
- V. V. KALMYKOV, V. E. BLOKHIN, and K. V. AGLITSKAYA. Tr. Voronezh. Gos. Univ. 73, 67 (1969); Chem. Abstr. 74, 47608 (1971).
- 4. A. MATHIAS. Mol. Phys. 12, 381 (1967).

- 5. B. J. MILLARD and A. F. TEMPLE. Org. Mass Spectrom. 1, 285 (1968).
- 6. F. M. HERSHENSON, L. BAUER, and K. F. KING. J. Org. Chem. 33, 2543 (1968).
- 7. T. KAMETANI, S. HIRATA, S. SHIBUYA, and M. SHIO. Org. Mass Spectrom. 4, 395 (1970).
- D. C. DEJONGH and G. N. EVENSON. J. Org. Chem. 37, 2152 (1972) and references therein.

- 9. H. R. SNYDER, C. T. ELSTON, and D. B. KEL-LOM. J. Am. Chem. Soc. 75, 2014 (1953).
- 10. D. HARRISON and A. C. B. SMITH. J. Chem. Soc. 3157 (1959).
- 11. L. S. EFROS and L. R. DAVIDENKOV. J. Gen. Chem. USSR 21, 2289 (1951).
- 12. K. NAKAGAWA and H. ONOUE. Chem. Commun. 396 (1965).
- J. G. GRASSELLI, B. L. ROSS, H. F. HUBER, and J. M. AUGL. Chem. Ind. (London), 162 (1963).
- H. R. SNYDER, K. C. MURDOCK, and C. S. MARVEL. J. Am. Chem. Soc. 75, 4742 (1953).
- J. A. ELVIDGE and P. SIMS. J. Chem. Soc. (C), 385 (1966).
- 16. G. H. JEFFREY, R. PARKER, and A. I. VOGEL. J. Chem. Soc. 570 (1961).
- Y. SUGIMOTO, S. NISHIMURA, and E. INOTO. Bull. Univ. Osaka, Prefecture Ser. A, 8, 71 (1959). Chem. Abstr. 55, 12029 (1961).
- K. R. JENNINGS. In Mass spectrometry: techniques and applications. Edited by G. W. A. Milne. Wiley Interscience, New York. 1971.
- 19. D. C. DEJONGH, S. C. PERRICONE, M. L. GAY, and W. KORYTNYK. Org. Mass Spectrom. 1, 151 (1968).
- C. D. CAMPBELL and C. W. REES. Chem. Commun. 192 (1965).
- 21. J. H. HALL. J. Am. Chem. Soc. 87, 1147 (1965).
- 22. J. C. TOU and R. M. RODIA. Org. Mass Spectrom. 6, 493 (1972).