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The Behavior of 1-Phenyl-2-benzimidazolinethione and 1-Phenyl-2-benzimidazolinone upon Electron Impact and Pyrolysis

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DENIS C. K. LIN, MICHAEL L. THOMPSON, and DON C. DEJONGH. Can. J. Chem. 52, 2359 (1974).

The mass spectra of 1-phenyl-2-benzimidazolinethione (**3**) and 1-phenyl-2-benzimidazolinone (**4**) have been compared with their pyrolysis products and similarities have been found. In the 70 eV mass spectrum of **3**, the base peak results from the loss of H•; at low ionizing voltages, this path and a competing path, loss of S, are the only ones which remain. At 650° in a stream of N_2, 1-phenylbenzimidazole (**8**, 20%) formed from the loss of S and benzimidazo-[2,1-*b*]benzothiazole (**5**, 11%) formed by loss of H_2. The major fragmentation paths in the mass spectrum of **4** are loss of CHO• and NCO•. At 950°, phenazine (**6**, 35%) formed by loss of CH_2O, and carbazole (**7**, 14%) formed by loss of HNCO. In each pyrolysis, 65–70% of the starting material was recovered or accounted for.

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On rapporte les spectres de masse de la phenyl-1 benzimidazolinethione-2 (**3**) et de la phenyl-1 benzimidazolinone-2 (**4**), tel qu'obtenus par impact électronique. On compare ces spectres avec les produits de pyrolyse des composés **3** et **4**. Dans le spectre de masse du composé **3**, pris à 70 eV, le pic de base se forme par perte de H•; à basses énergies des électrons, ce dernier est accompagné de l'ion moléculaire ainsi que d'un pic résultant de l'élimination de S. La pyrolyse du composé **3** à 650° dans un courant d'azote conduit à la formation de phenyl-1 benzimidazole (**8**, 20%) par perte de S et à la formation de benzimidazo[2,1-*b*]benzothiazole (**5**, 11%) par perte de H_2. Les patrons majeurs de fragmentation trouvés dans le spectre de masse du composé **4** résultent de la perte de CHO• et de la perte de NCO•. Les produits de la pyrolyse du composé **4** à 950° sont la phénazine (**6**, 35%) formée par la perte de CH_2O et le carbazole (**7**, 14%) formé par la perte de HNCO. Dans chaque cas, les produits formés ainsi que les produits originaux récupérés représentent de 65 à 70% des produits de départ.

Introduction

A considerable number of publications have appeared on the subject of pyrolysis at short contact times in the gas phase (1) and several of them have included a comparison of the pyrolysis products with those products which would be expected from an interpretation of the mass spectra of the starting material. We have been working in this area for several years (2) and report some of our recent results in this article.

A project under study in our laboratory is a comparison of the mass spectra and pyrolyses of molecules related to benzothiazole, benzoxazole, and benzimidazole (2, 3). Results obtained from 2-benzimidazolinethione (**1**) and 2-benzimidazolinone (**2**) were included in our recent reports (2, 3). Now, we have observed from the mass spectra of their *N*-phenyl deriva-

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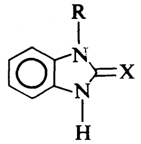


1 X = S: R = H **3** X = S; R = C_6H_5
2 X = O; R = H **4** X = O; R = C_6H_5

tives (**3** and **4**) that the phenyl group has a major influence on fragmentation of the molecular ions of these compounds. This observation has led us to study the pyrolyses of **3** and **4** in order to see if this influence is also important there.

In this article we report the mass spectrum, photolysis, and pyrolysis of 1-phenyl-2-benzimidazolinethione (**3**) and the mass spectrum and pyrolysis of 1-phenyl-2-benzimidazolinone (**4**). The mass spectrum of **4** has been published previously (4). High-resolution data and metastable-ion peaks are discussed in the schemes and text, along with certain features of the spectra obtained at low ionizing voltages.

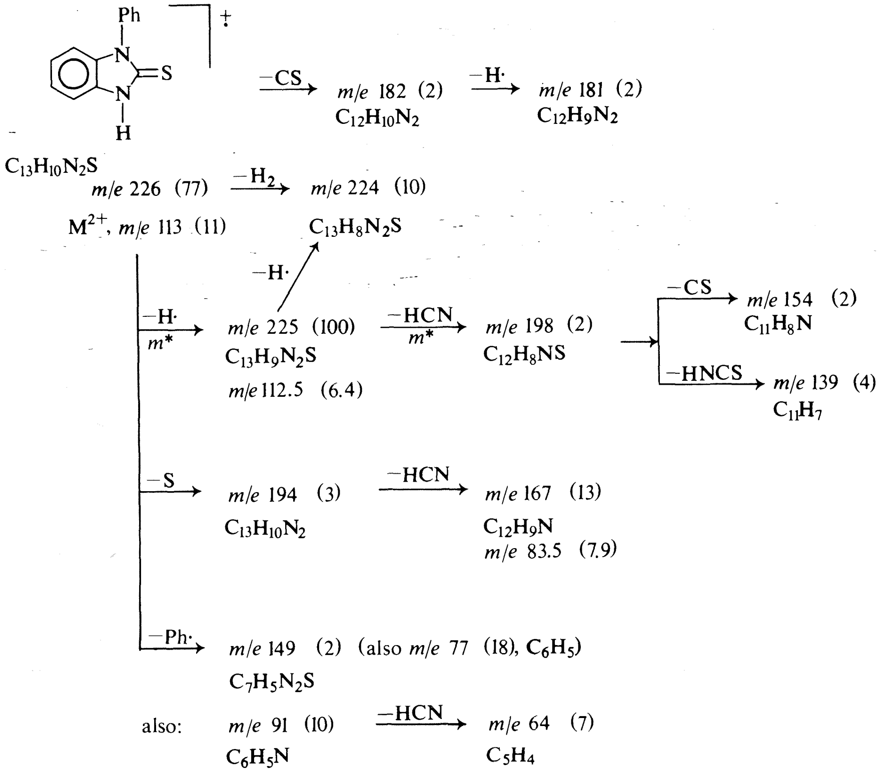
Infrared spectra and dipole moments provide evidence for the presence of the keto structure of **2** (5). Thus, we will use the keto and thioketo forms in our discussion, rather than the tautomeric enol and thiol forms, even though there is no evidence that either form is preferred in the molecular ions.

Pyrolyses were performed by sublimation of the samples into a stream of N_2 which passed through an unpacked quartz tube surrounded by a 12 in. furnace (3, 6). Generally, a N_2 flow rate of 0.25 l/min and a system pressure of about 2 Torr were used. The pyrolyses were repeated several times at the same and different temperatures. Where possible, pyrolysis products were isolated and identified by physical as well as spectroscopic characteristics.

Results

1-Phenyl-2-benzimidazolinethione (3)

The 70 eV mass spectrum of **3** is summarized in Scheme 1. The (M − H) peak is the base peak



Scheme 1[2]

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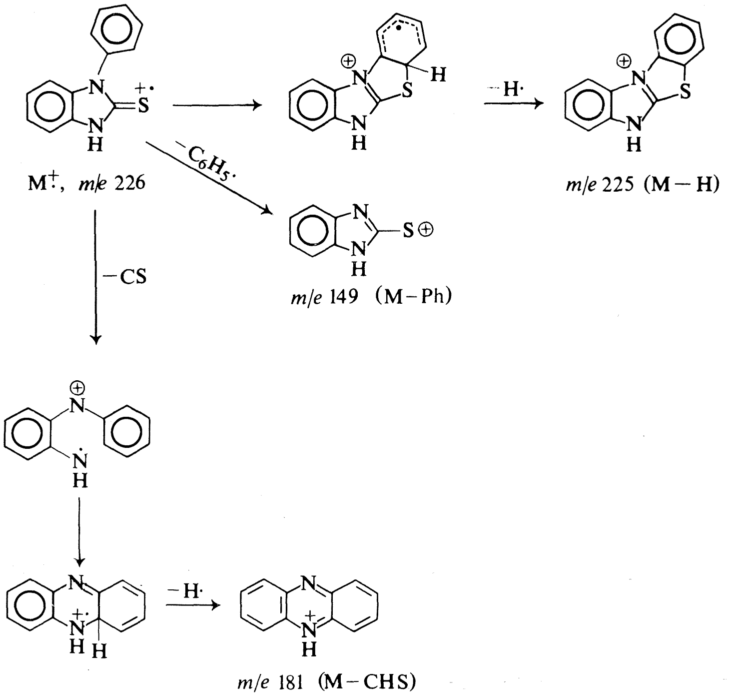
[2] The elemental compositions are the result of exactmass measurements. The values in parentheses are relative intensities and m^* denotes the presence of a metastable-ion peak.



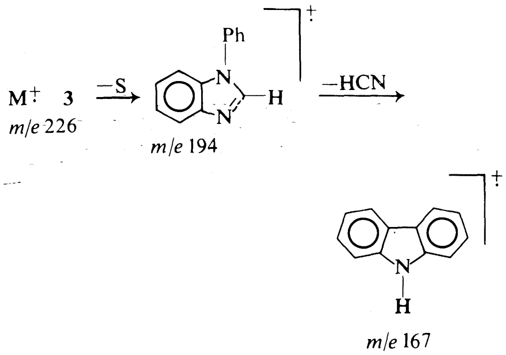
SCHEME 2

at 15 eV as well as at 70 eV. The peaks at *m/e* 224 (M − 2H) and at *m/e* 194 (M − S) are the only other fragment-ion peaks found at 15 eV. In fact, the peak at *m/e* 194 is present at electron voltages as low as 12 eV. Minor paths found at 70 eV begin by the loss of CS and by the loss of $C_6H_5\cdot$. An abundant loss of H· is not observed in the mass spectrum of **1**; however in that case the loss of S is the lowest-energy path (3). There is no metastable-ion peak for formation of the peak at *m/e* 224 either from the peaks at *m/e* 226 or 225. So, it cannot be determined that the peak at *m/e* 224 forms by a one-step and/or a two-step path.

The fragmentations proposed in Scheme 2 can account for the formation of these ions. The structure proposed for the ion at *m/e* 225 corresponds to the protonated form of benzimidazo[2,1-*b*]benzothiazole (**5**) and the structure proposed for the ion at *m/e* 181 corresponds to protonated phenazine (**6**). The peak at *m/e* 194 can be represented by the molecular ions of 1- and/or 2-phenylbenzimidazole (**8** and **9**). The loss of HCN from *m/e* 194 could give the molecular ion of carbazole (**7**) at *m/e* 167 (eq. 1).

Compound **3** was pyrolyzed at 650, 800, and 950°. At 650°, 46.5% of starting compound was

[1]

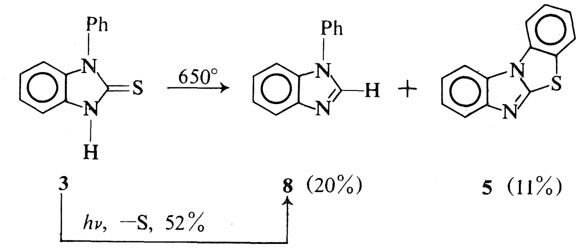


recovered. In addition, a 20% yield (based on unrecovered **3**) of 1-phenylbenzimidazole (**8**) and an 11% yield of benzimidazo[2,1-*b*]benzothiazole (**5**) were obtained (eq. 2).

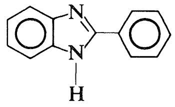
Compound **8** forms by loss of S from **3** with migration of H from N to C. In the formation of **5**, the phenyl ring becomes bonded to the sulfur atom and H_2 is lost.

At 950°, the recovery of **3** decreased to 23.1% and the yield of **5** increased to 24%. On the other hand, the yield of **8** decreased to <0.5% but carbazole (**7**, 3%) and 2-phenylbenzimidazole (**9**, 11%) were now present among the pyrolysis products. Trace amounts of phenazine (**6**),

[2]



cyanocarbazole, 1- and 2-cyanonaphthalenes, 2-cyanoaniline, naphthalene, and benzonitrile were identified in addition.



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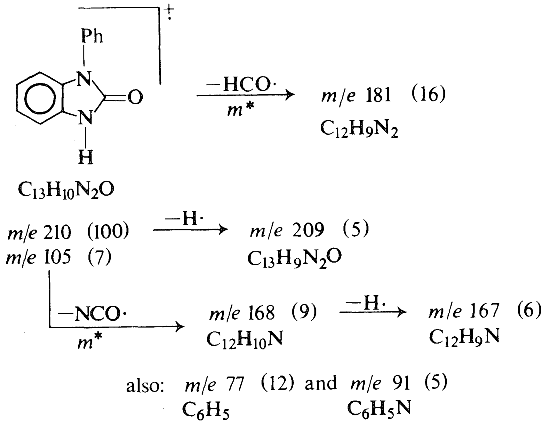
Also we photolyzed **3** in order to compare its behavior with the results obtained upon pyrolysis and electron impact. The only product found was 1-phenylbenzimidazole (**8**), formed by the loss of S, in 52% yield. *t*-Butyl alcohol was used as the solvent.

In summary, the lowest energy fragmentations of **3** upon electron impact are loss of H· and loss of S from the molecular ions. Pyrolysis of **3** at 650° produces benzimidazo[2,1-*b*]benzothiazole (**5**) by a loss of H_2 and 1-phenylbenzimidazole (**8**) by loss of S. Only compound **8** is observed upon photolysis of **3** in *t*-butyl alcohol.

1-Phenyl-2-benzimidazolinone (4)

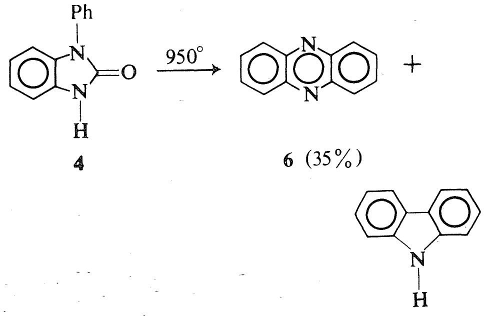
The 70 eV mass spectrum of **4** is summarized in Scheme 3. The major fragmentation paths begin with loss of HCO· and with loss of NCO·. There are broad metastable-ion peaks present for each of these fragmentations. At 12 eV, the relative intensities of *m/e* 181 and 168 are 6 and 4%, respectively; also, there are very minor peaks present at *m/e* 209 and 167. The ions at *m/e* 181 can be represented as protonated phenazine and those at *m/e* 168 and 167 as protonated carbazole and carbazole (**7**), respectively.



SCHEME 3

Compound **4** was pyrolyzed at 950° and 16.3% was recovered. The major products and their yields (based on unrecovered starting material) were phenazine (**6**, 35%) and carbazole (**7**, 14%) (eq. 3).

[3]



7 (14%)

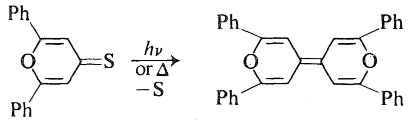
A number of minor products were obtained also, *viz.* diphenylamine (1%), 1- and 2-cyanonaphthalenes (2.5%), naphthalene (2%), benzonitrile (3%), and phenylisocyanate (2%). The last product was isolated as *N*-phenylcarbamate, after having reacted with ethanol during the work-up.

In summary, compound **4** loses CHO· and NCO· in the mass spectrometer. Pyrolysis of **4** gives phenazine, after loss of CH_2O (probably as CO and H_2) and carbazole, after loss of HNCO.

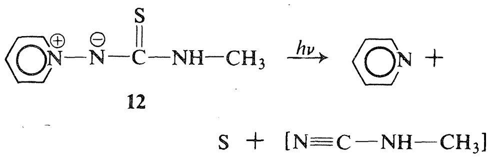
Discussion

At low ionizing voltages only two decompositions of the molecular ions of **3** are observed: loss of S and loss of H·. The products formed in the pyrolysis of **3** can be explained by similar decompositions. The formation of 1-phenylbenzimidazole (**8**) can arise by a desulfurization of the C═S bond; there is a neighboring hydrogen which can rearrange to the developing electron-deficient center. Compound **8** is a major product isolated from the pyrolysis of **3** and the only product isolated from photolysis in *t*-butyl alcohol.

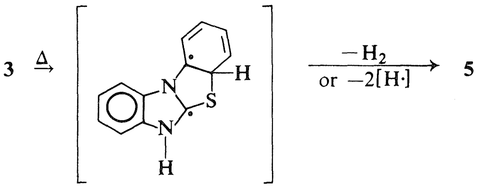
Precedents can be found for the pyrolytic and photolytic desulfurization of the C═S bond. For example, 2,6-diphenyl-4*H*-pyran-4-thione (**10**) undergoes photodesulfurization, giving the dimer **11** in 80% yield, (eq. 4) (7). This dimerization with desulfurization was also observed upon the heating of **10**. Another example, 1-(3-methyl-2-thioureido)pyridinium hydroxide inner salt (**12**) gives, in practically quantitative yield, pyridine and sulfur, (eq. 5) (8). Methyl cyanamide has been proposed as the undetected component. An initial loss of sulfur has been proposed as the most likely pathway. The molecular ion of **12** loses sulfur giving an ion $C_7H_9N_3$ which readily forms the pyridinium ions at *m*/*e* 79 by losing the elements of methyl cyanamide. Thus, the mass-spectral fragmentation pattern is consistent with the photochemical reaction.

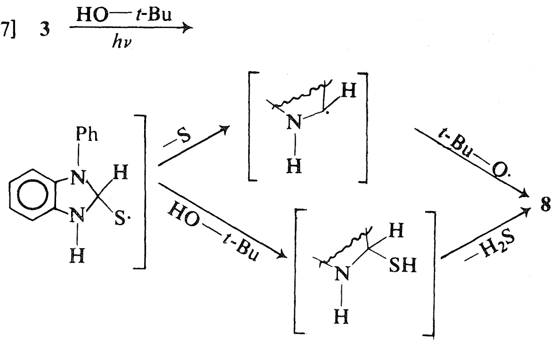
[4]


10 **11**

[5]


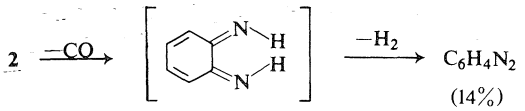
The other product (**5**) formed in the pyrolysis of **3** results from the addition of the thermally excited thioketo group to the aromatic ring (eq. 6). The photoaddition of thiocarbonyl compounds to olefins is well known (9). Also, **8** could be formed photolytically from **3** in *t*-butyl alcohol by the photoexcitation of the thiocarboxyl group, (eq. 7). A similar scheme has been proposed to explain the photoreduction reactions of thiobenzophenones in solvents which have easily extractable hydrogens (10). In the photodimerization with elimination of sulfur of 4*H*-pyran-4-thiones, the presence of H_2S was detected (7*b*).

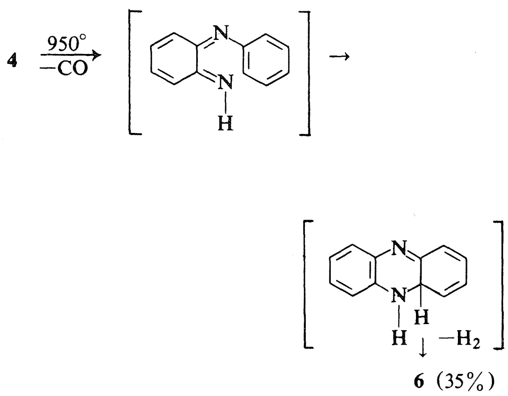
[6]


[7]


In comparison, pyrolysis of **1** at 950° gave a 70% yield of products resulting from the loss of S (3). The loss of S from the molecular ions and from the (M + H) ions in the chemical-ionization mass spectrum is the lowest-energy fragmentation. The major pyrolysis product is benzimidazole (**8**, NH in place of N—Ph) (62.5%); this isomerizes to 2-cyanoaniline (7.5%) under the pyrolytic conditions. There is no pathway for **1** which is similar to the loss of H· from the molecular ions of **3** or to the formation of **5** from **3**.

At 1000°, 2-benzimidazolinone (**2**) gave a 14% yield of $C_6H_4N_2$ isomers, resulting from the loss of CO and H_2. The intermediate shown in eq. 8 was invoked to explain these results (2). The major product isolated from the pyrolysis of **4** can be explained by the same type of intermediate. However, in this case an internal cyclization occurs before the H_2 is lost (eq. 9). The loss

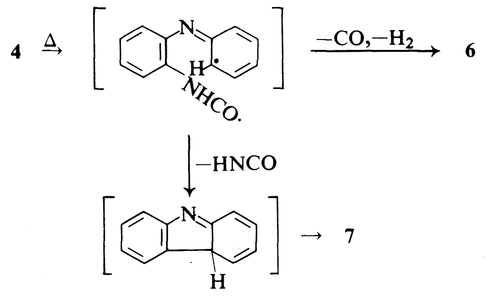
[8]


[9]


of CHO· is one of the two major fragmentation pathways in the mass spectrum of **4**. Decarbonylation under pyrolytic conditions has frequently been observed. (1, 2).

The other product, carbazole (**7**), formed in 14% yield in the pyrolysis of **4** is the result of the loss of HNCO. Also, a major fragmentation in the mass spectrum of **4** is the loss of NCO·. To explain the formation of **7**, the initial cleavage of the carbonyl carbon – *N*-phenyl bond can be proposed (eq. 10). If the phenyl group participates in the loss of HNCO, **7** can be formed. On the other hand, decarbonylation leads to the reactions shown in eq. 9.

[10]



The compounds **3** and **4** therefore join the list of compounds (1–3) whose pyrolytic and electron-impact fragmentations are similar. The lowest-energy paths in their mass spectra can be compared with the pyrolysis products. The reactions seem to be governed by the elimination of small, neutral species such as CO, S, H_2, and HNCO. The *N*-phenyl group intramolecularly traps reactive intermediates to give stable polycyclic products in relatively high yields, a path which is not available to compound **1** and **2**. In each pyrolysis, 65–70% of the starting material was accounted for.

These and other similarities among high-energy processes provide possibilities of finding useful synthetic applications and evidence for novel reaction intermediates, as well as the possibility of studying interesting decomposition pathways.

Experimental Section

Melting points were determined by the open capillary method using a MEL-TEMP apparatus and were corrected. Infrared spectra were recorded with a Beckman IR8 spectrometer and a Perkin-Elmer Infracord. Nuclear magnetic resonance spectra were taken on a Varian T-60 spectrometer using 1% TMS as an internal standard. Ultraviolet spectra (1 cm path) were determined on a Bausch and Lamb 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 ±0.0015 mass units. Metastable ions were observed in the low-resolution spectra and, in certain cases, sought with the AEI MS-902 spectrometer operating in the defocused mode.

The ion source of the RMU-6D was maintained at 250° and the MS-902, at 150°. Since pyrolysis of the compounds studied does not begin until approximately 600°, pyrolysis in the source cannot account for the fragmentations observed.

The gas-chromatographic (g.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 10 g.c. 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. Analysis were performed by Midwest Microlab, Inc., Indianapolis, Indiana.

Chemicals

2-Aminodiphenylamine, benzotriazole, 2-phenylbenzimidazole (**9**), phenazine (**6**), 1-cyanoaniline, and benzonitrile were purchased from Aldrich; 1- and 2-cyanonaphthalene were purchased from Eastman Kodak; carbazole (**7**), diphenylamine, and naphthalene were purchased from Fisher.

1-Phenyl-2-benzimidazolinethione (3)

Compound **3** was prepared by modifying a procedure published by Allen and Deacon (11). A mixture of 18.8 g of 2-aminodiphenylamine, 18.4 g of potassium ethyl xanthate, 100 ml of ethanol, and 20 ml of H_2O was refluxed with stirring for 3 h. After the first 10 min of refluxing, 4 g of carbon was added cautiously to the ethanol solution. The hot reaction mixture was filtered by gravity to remove the carbon. Approximately 500 ml of warm H_2O and 10 ml of glacial acetic acid were added to the ethanolic solution. The off-white crystals were recrystallized from ethanol, yielding 12 g of 1-phenyl-2-benzimidazolinethione (**3**): m.p. 196–197° (lit. (12) 194°); yield 52%. The i.r. spectrum ($HCCl_3$) contains absorption bands at 3475, 2350, and 1217 cm^{-1}. The mass spectrum is summarized in Scheme 1 and discussed in the text.

Anal. Calcd. for $C_{13}H_{10}N_2S$: C, 69.03; H, 4.42. Found: C, 69.32; H, 4.47.

1-Phenyl-2-benzimidazolinone (4)

Compound **4** was prepared from 2-aminodiphenylamine by the procedure of Simonov and Pozhanskii (13). Toluene was used for recrystallization; yield: 5.0 g, (34%); m.p. 202–203° (lit. (13, 14) m.p. 202–203°); i.r.

TABLE 1. Pyrolyses of 1-phenyl-2-benzimidazolinethione (**3**)*

	% recovered at		
	650°	800°	950°
1-Phenyl-2-benzimidazolinethione (**3**)	46.5	37.0	23.1
(Starting amount of **3**, g)	(0.80 and 1.27)	(1.41 and 1.46)	(1.01, 1.14, and 1.82)
Benzimidazo[2,1-*b*]benzothiazole (**5**)	6.0	15.0	18.7
2-Phenylbenzimidazole (**9**)	—	<0.5	8.7
Cyanocarbazole	—	<0.5	2.0
1-Phenylbenzimidazole (**8**)	10.8	5.9	<0.5
Carbazole (**7**)	—	1.0	2.3
Phenazine (**6**)	—	Trace	<0.5
1-Cyanonaphthalene	—	Trace	1.2
2-Cyanonaphthalene	—	Trace	0.7
2-Cyanoaniline	—	<0.5	2.5
Naphthalene	—	Trace	1.0
Benzonitrile	—	<0.5	3.7
Total	63.3	60.9	64.9

*A N_2 flow rate of 0.20–0.25 l/min and system pressure of 0.7–2.0 Torr were used.

spectrum ($HCCl_3$) contains absorption bands at 3390, 3060, 1705, 1600, 1500, and 1380 cm^{-1}.

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.29; H, 4.76. Found: C, 74.12; H, 5.01.

1-(2-Benzothiazolyl)benzotriazole

1-(2-Benzothiazolyl)benzotriazole was prepared from benzotriazole by the method used by Orth and Soedigdo (15); yield 4.3 g (34%); m.p. 174° (lit. (15) m.p. 174°); λ_{max} (EtOH) 322, 275 sh, 268, 245, and 228.5 nm.

Anal. Calcd. for $C_{13}H_8N_4S$: C, 61.89; H, 3.19; N, 22.21; S, 12.71. Found: C, 61.68; H, 3.33; N, 22.36; S, 13.05.

Benzimidazo[2,1-b]benzothiazole (5)

Benzimidazo[2,1-b]benzothiazole (**5**) was prepared photolytically from 1-(2-benzothiazolyl)benzotriazole (1 g) according to the method of Hubert (16) using a 450 W high-pressure Hg lamp; yield, 0.17 g (18%); λ_{max} (EtOH) 300, 291, 283, 263 sh, 242, and 222 nm; mass spectrum, *m/e* 224 ($C_{13}H_8N_2S$, 100), 223 ($C_{13}H_7N_2S$, 16), 198 ($C_{12}H_8NS$, 8), 192 ($C_{13}H_8N_2$, 3), 180 ($C_{12}H_8N_2$, 3), 179 ($C_{12}H_7N_2$, 5), 166 ($C_{12}H_8N$, 3), 134 (C_7H_4NS, 3), 122 (C_6H_4NS, 6), 112 ($C_{13}H_8N_2S$ (doubly charged), 30), 96 (C_5H_4S, 10), and 90 (C_6H_4N, 8); molecular ion, *m/e* 224.0405. Calcd. for $C_{13}H_8N_2S$, *m/e* 224.0408.

Pyrolysis Apparatus and Procedure

The pyrolysis apparatus and procedure have been described previously (3, 6). The sample (approximately 1 g) in a stream of nitrogen passed through a quartz tube heated by an electric furnace 12 in. long. The flow rate was 0.25 l/min at 2.5 Torr. A series of traps was placed between the quartz tube and the pump. Approximately 1 h was required for the passage of each $\frac{1}{2}$ g of sample through the tube. A solution was made of the material in the traps in a volumetric flask; g.l.p.c. and t.l.c. were used to separate the compounds in this solution.

Photolysis Apparatus and Procedure

The apparatus (Hanovia) used for photolysis consisted of a quartz immersion well, a 450 W high-pressure mercury lamp, an appropriate power supply, various filters, and a 500 ml reaction-vessel jacket. The compounds were dissolved in appropriate solvents and placed in the reaction vessel. During photolysis the apparatus was cooled by running water through the immersion well. The reactions were followed by the u.v. spectrum of the reaction solutions. The photolysis was stopped when no more changes in the u.v. spectrum were observed. Then the solvent of a measured amount of reaction solution was evaporated off in vacuum and the residue was made into a solution in a volumetric flask for analysis.

Pyrolysis of 1-Phenyl-2-benzimidazolinethione (3)

The conditions and results for the pyrolyses of 1-phenyl-2-benzimidazolinethione (**3**) are summarized in Table 1. The percentages shown are averages of different trials at the same temperature; good agreement was obtained among the different runs.

In each case, three traps were employed: the first was air cooled and the next two were cooled with liquid nitrogen. The traps were washed with acetone and chloroform. The g.c. column used was 6 ft, 10% SE 54 on Chromosorb G 60/80. The cyanonaphthalenes were better separated on a 6 ft column of 3% OV 225 on Chromosorb W 80/100. The temperature was programmed between 100° (1 min) and 260° (hold) at 10°/min. The column used for g.c./m.s. was a 6 ft glass column of 3% OV1 Chrom HP 80/100. The starting material did not elute from the g.c. columns well and was recovered by extracting all the other compounds using heptane from the residue of a known amount of the pyrolysis solution. The concentration of 1-phenylbenzimidazole (**8**) was estimated from u.v. data (17). The exact position of the cyano group on the cyanocarbazole ring was not determined; analysis by g.c. showed that it had a different retention time from 9-cyanocarbazole, which was synthesized for comparison (18). The concentration of cyanocarbazole was estimated using carbazole (**7**) as a standard. All other products were identified by comparison with authentic materials. 2-Cyanoaniline had a tendency to react on standing with acetone to form an anil, *o*-cyano-*N*-isopropylideneaniline.

Photolysis of 1-Phenyl-2-benzimidazolinethione (3)

1-Phenyl-2-benzimidazolinethione (0.2 g) in 400 ml of *t*-butyl alcohol was used for photolysis. A Vycor filter was used. The reaction was stopped after an irradiation time of 1 h. A quantity of 300 ml of reaction solution was evaporated to make up a 25 ml solution using chloroform. Analysis by g.c. was made using a 6 ft column, 10% SE 54. The only product was 1-phenylbenzimidazole (**8**). The yield was estimated to be 51.8% from its u.v. absorption.

Pyrolysis of 1-Phenyl-2-benzimidazolinone (4)

The temperature used in the pyrolyses of 1-phenyl-2-benzimidazolinone (4) was 950°. The N_2 flow rate was 0.20–0.25 l/min. The system pressure was 0.5–2.5 Torr. The columns used for g.c. analysis were the same as those used in the analysis of the pyrolyses of **3**. The average percentages of the products recovered from the two runs (0.94 and 1.26 g of starting material (**4**)) were: 1-phenyl-2-benzimidazolinone (**4**), 16.3%; phenazine (**6**), 29.6%; carbazole (**7**), 12.0%; diphenylamine, 0.7%; 1-cyanonaphthalene, 1.1%; 2-cyanonaphthalene, 0.9%; ethyl *N*-phenylcarbamate, 2.0%; naphthalene, 1.8% and benzonitrile, 2.4%. The total percentage recovered was 66.8%. Agreement between the two runs was good. Ethyl *N*-phenylcarbamate was synthesized for comparison by mixing phenylisocyanate (Matheson, Coleman and Bell) with excess absolute ethanol which then was left to evaporate at room temperature. The ethyl *N*-phenylcarbamate was recrystallized in hexane (m.p. 53°, (lit. (19) m.p. 53°)). All the other products were identified by comparison with authentic materials and their concentrations, including starting material (**4**), were estimated by g.c.

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